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THEORETICAL STUDY OF THE RADIATIVE AND KINETIC PROPERTIES OF SELECTED METAL OXIDES AND AIR MOLECULES

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Technical Report

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A theoretical research program directed toward the study of the energetics and LWIR radiative properties of selected uranium/oxygen band systems has been undertaken. Included in this research program were the investigation of the strongest electronic and vibrational bands in the LWIR region for the species UO, UO^+, UO_2, UO_2^+, and UO_2^{++}. The program for accomplishing this research effort was formulated into three separate tasks: a) adaption of our electronic structure codes to the

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20. ABSTRACT (Continued)

DNA CYBER 76 System, b) calculation of pertinent electronic wavefunctions and energies, as a function of internuclear separation and within a relativistic framework, for selected species of the uranium/oxygen system which may be important in the LWIR region, and c) calculation of electronic transition moments and transition probabilities between specific vibrational levels of the electronic states corresponding to the strongest radiating band systems belonging to the uranium/oxygen system and prediction of IR and possible optical oscillator strengths.

Our calculations indicate that the species UO^+ will be efficiently solar pumped and will exhibit strong radiation in the region $0.6 \lesssim \lambda \lesssim 1.13$ µ. Further, we predict efficient conversion of solar photons to IR photons for this species. For UO_2^+, very strong solar pumping is predicted for $\lambda \lesssim 0.5$ µ. The pathways for conversion of solar photons to the LWIR region are still uncertain but strong LWIR radiation ($f_{01} \sim 10^{-4}$) is predicted for the vibrational transitions of the ground $^2\Phi_u$ state of UO_2^+. Further studies of UO_2^+ and examination of the relative importance of the doubly ionized species (U^{++}, UO^{++}, UO_2^{++}) in this system are indicated.

SUMMARY

A theoretical research program directed toward the study of the energetics and LWIR radiative properties of selected uranium/oxygen band systems has been undertaken. Included in this research program was the investigation of the strongest electronic and vibrational bands in the LWIR region for the species UO, UO^+, UO_2, UO_2^+, and UO_2^{++}. The program for accomplishing this research effort was formulated into three separate tasks: a) adaption of our electronic structure codes to the DNA CYBER 76 System, b) calculation of pertinent electronic wavefunctions and energies, as a function of internuclear separation and within a relativistic framework, for selected species of the uranium/oxygen system which may be important in the LWIR region, and c) calculation of electronic transition moments and transition probabilities between specific vibrational levels of the electronic states corresponding to the strongest radiating band systems belonging to the uranium/oxygen system and prediction of IR and possible optical oscillator strengths.

Our calculations indicate that the species UO^+ will be efficiently solar pumped and will exhibit strong radiation in the region $0.6 \lesssim \lambda \lesssim 11.3 \mu$. Further, we predict efficient conversion of solar photons to IR photons for this species. For UO_2^+, very strong solar pumping is predicted for $\lambda \lesssim 0.5 \mu$. The pathways for conversion of solar photons to the LWIR region are still uncertain but strong LWIR radiation ($f_{01} \sim 10^{-4}$) is predicted for the vibrational transitions of the ground $^2\Phi_u$ state of UO_2^+. Further studies of UO_2^+ and examination of the relative importance of the doubly ionized species (U^{++}, UO^{++}, UO_2^{++}) in this system are indicated.

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PREFACE

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INTRODUCTION

The release of certain chemical species into the upper atmosphere results in luminous clouds that display the resonance electronic-vibration-rotation spectra of the chemically reacting species. Such spectra are seen in rocket releases of chemicals for upper atmospheric studies, upon re-entry into the atmosphere of artificial satellites and missiles, and as a result of energy deposition in the atmosphere caused by nuclear weapons effects. Of particular interest in this connection is the observed spectra of certain metallic oxides. From band intensity distributions of the spectra, and knowledge of the f-values for electronic and vibrational transitions, the local conditions of the atmosphere can be determined (Reference 1). Such data are fundamental for the analysis of detection and discrimination problems.

Present theoretical efforts, which are directed toward a more complete and realistic analysis of the transport equations governing atmospheric relaxation and the propagation of artificial disturbances, require detailed information of thermal opacities and LWIR absorption in region of temperature and pressure where both atomic and molecular effects are important (References 2 and 3). Although various experimental techniques have been employed for both atomic and molecular systems, theoretical studies have been largely confined to an analysis of the properties (bound-bound, bound-free and free-free) of atomic systems (References 4 and 5). This has been due in large part to the unavailability of reliable wavefunctions for diatomic molecular systems, and particularly for excited states or states of open-shell structure. Only recently (References 6-8) have reliable procedures been prescribed for such systems which have resulted in the development of practical computational programs.

The application of these computational methods to studies of the electronic structure and radiation characteristics of metal oxides has been reported for several of the lighter systems (References 9-11). A preliminary study of the uranium/oxygen system has been reported by Michels (Reference 12) which identified a large number of low-lying molecular states for both the

UO and UO^+ systems. Of particular interest was the discovery of two structures for UO^+ that resulted from two different spin-couplings of the uranium valence electrons. These results suggested strong LWIR radiation in UO^+ arising from different electronic state transitions.

An inherent uncertainty in these preliminary calculations was present, owing to the neglect of relativistic effects that were much too difficult to include in molecular calculations at that period of time. The 7s valence electron of uranium, and its corresponding σ-bonding molecular orbital, are highly relativistic in nature which results in a contracted charge density relative to that which would occur in lighter molecular systems. The effect of this contraction on the relative positions of the low-lying electronic states of the uranium/oxygen system can now be calculated with some degree of confidence using newly developed relativistic computer codes.

Because of inherent difficulties in the experimental determination of the spectroscopy, transition probabilities and LWIR radiation for metal oxide systems and in light of the aforementioned recent progress in the calculation of relativistic electronic wavefunctions, especially for diatomic systems, a technical program for calculating these properties was undertaken for the Defense Nuclear Agency under Contract DNA001-82-C-0015. The emphasis in this work was on the ions of uranium and uranium oxides (U^+, UO^+, UO_2^+) since these have been determined to be important radiators in the LWIR region. These studies indicated that the doubly ionized species, U^{++}, UO^{++} and UO_2^{++}, should also be considered because of their role in charge neutralization processes and their potential as early-time radiators.

The general composition of this report is as follows. In Section II, we present a description of the mathematical methods which were employed in this research. Included in Section II are sub-sections which deal with the construction of electronic wavefunctions, the calculations of expectation properties, the evaluation of molecular transition probabilities, and the calculation of electronic wavefunctions using both the ab initio and density functional methods. This is followed by Section III which describes the inclusion of relativistic effects into the density functional (X_α) method. The calculated results and pertinent discussion are presented in Section IV. Recommendations are presented in Section V.

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METHOD OF APPROACH - NONRELATIVISTIC METHODS

A. QUANTUM MECHANICAL CALCULATIONS

Central to these theoretical studies are the actual quantum-mechanical calculations which must be carried out for the atomic and molecular species. For added clarity, various aspects of these calculations are discussed in individual subsections.

1. Levels of Approximation

Much evidence on diatomic and polyatomic systems indicates the inadequacy of a minimum Slater-type-orbital (STO) basis for constructing quantitatively correct molecular wavefunctions (References 13 and 14). This means inner-shell and valence-shell STO's of quantum numbers appropriate to the atoms (1s, 2s, 2p, for C, N, O; etc.). The main deficiency of the minimum basis set is in its inability to properly describe polarization and the change of orbital shape for systems which exhibit large charge transfer effects. Values of the screening parameters ζ for each orbital can either be set from atomic studies or optimized in the molecule; the latter approach is indicated for studies of higher precision. When high chemical accuracy is required, as for the detailed studies of the ground or a particular excited state of a system, a more extended basis must be used. Double-zeta plus polarization functions or optimized MO's are required for reliable calculated results of chemical accuracy.

The chosen basis sets give good results only when used in a maximally flexible manner. This implies the construction of CI wavefunctions with all kinds of possible orbital occupancies, so that the correlation of electrons into overall states can adjust to an optimum form at each geometrical conformation and for each state. Except when well-defined pairings exist, as for closed shell and exchange dominated systems, a single-configuration study (even of Hartree-Fock quality) will be inadequate.

2. Spin and Symmetry

Proper electronic states for systems composed of light atoms should possess definite eigenvalues of the spin operator S^2 as well as an appropriate geometrical symmetry. The geometrical symmetry can be controlled by the assignment of orbitals to each configuration, but the spin state must be

obtained by a constructive or projective technique. Formulas have been developed (Reference 15) for projected construction of spin states from orthogonal orbitals, and programs implementing these formulas have been in routine use at UTRC for several years.

One of the least widely appreciated aspects of the spin-projection problem is that the same set of occupied spatial orbitals can sometimes be coupled to give more than one overall state of given S quantum number. It is necessary to include in calculations all such spin couplings, as the optimum coupling will continuously change with changes in the molecular conformation. This is especially important in describing degenerate or near-degenerate excited electronic states.

3. Method of Ab Initio Calculation

A spin-free, nonrelativistic, electrostatic Hamiltonian is employed in the Born-Oppenheimer approximation. In systems containing atoms as heavy as Kr, this approximation is quite good for low-lying molecular states. For a diatomic molecule containing n electrons, the approximation leads to an electrostatic Hamiltonian depending parametrically on the internuclear separation, R:

$$\mathcal{H}(R) = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Z_A}{r_{iA}} - \sum_{i=1}^{n} \frac{Z_B}{r_{iB}} + \frac{Z_A Z_B}{R} + \sum_{i>j\geq1}^{n} \frac{1}{r_{ij}} \qquad (1)$$

where Z_A and Z_B are the charges of nuclei A and B, and r_{iA} is the separation of electron i and nucleus A. $\mathcal{H}$ is in atomic units (energy in hartrees, length in bohrs).

Electronic wavefunctions $\psi(R)$ are made to be optimum approximations to solutions, for a given R, of the Schrödinger equation

$$\mathcal{H}(R)\,\Psi(R) = E(R)\,\Psi(R) \qquad (2)$$

by invoking the variational principle

$$\delta W(R) = \delta \, \frac{\int \Psi^*(R)\mathcal{H}(R)\Psi(R)\,d\tau}{\int \Psi^*(R)\Psi(R)\,d\tau} \qquad (3)$$

The integrations in Equation (3) are over all electronic coordinates and the stationary values of W(R) are approximations to the energies of states described by the corresponding $\psi(R)$. States of a particular symmetry are studied by restricting the electronic wavefunction to be a projection of the appropriate angular momentum and spin operators. Excited electronic states corresponding to a particular symmetry are handled by construction of configuration-interaction wavefunctions of appropriate size and form.

The specific form for $\psi(R)$ may be written

$$\Psi(R) = \sum_{\mu} c_{\mu} \Psi_{\mu}(R) \tag{4}$$

where each $\psi_{\mu}(R)$ is referred to as a configuration, and has the general structure

$$\Psi_{\mu}(R) = \mathcal{A} \mathcal{O}_s \prod_{i=1}^{n} \Psi_{\mu i}(r_i, R) \theta_M \tag{5}$$

where each $\phi_{\mu i}$ is a spatial orbital, $\mathcal{A}$ is the antisymmetrizing operator, $\mathcal{O}_s$ is the spin-projection operator for spin quantum number S, and θ_M is a product of α and β one-electron spin functions of magnetic quantum number M. No requirement is imposed as to the double occupancy of the spatial orbital, so Equations (4) and (5) can describe a completely general wavefunction.

In Hartree-Fock calculations $\psi(R)$ is restricted to a single ψ_{μ} which is assumed to consist as nearly as possible of doubly-occupied orbitals. The orbitals $\phi_{\mu i}$ are then selected to be the linear combinations of basis orbitals best satisfying Equation (3). Writing

$$\phi_{\mu i} = \sum_{\nu} a_{\nu i} \chi_{\nu} \tag{6}$$

the $a_{\nu i}$ are determined by solving the matrix Hartree-Fock equations

$$\sum_{\nu} F_{\lambda \nu} a_{\nu i} = \epsilon_i \sum_{\nu} S_{\lambda \nu} a_{\nu i} \quad \text{(each } \lambda \text{)} \tag{7}$$

where ϵ_i is the <u>orbital</u> energy of $\phi_{\mu i}$.

The Fock operator $F_{\lambda\nu}$ has been thoroughly discussed in the literature (Reference 16) and depends upon one- and two-electron molecular integrals and upon the $a_{\nu i}$. This makes Equation (7) nonlinear and it is therefore solved iteratively. UTRC has developed programs for solving Equation (7) for both closed and open-shell systems, using basis sets consisting of Slater-type atomic orbitals. Examples of their use are in the literature (Reference 7).

In configuration interaction calculations, the summation of Equation (4) has more than one term, and the $\underset{\sim}{c}_\mu$ are determined by imposing Equation (3) to obtain the secular equation

$$\sum_\nu (H_{\mu\nu} - w S_{\mu\nu}) c_\nu = 0 \qquad (\text{each } \mu) \qquad (8)$$

where

$$H_{\mu\nu} = \int \Psi_\mu^* (R) \mathcal{H}(R) \Psi_\nu (R) \, d\tau$$

$$S_{\mu\nu} = \int \Psi_\mu^* (R) \Psi_\nu (R) \, d\tau \qquad (9)$$

Equation (8) is solved by matrix diagonalization using either a modified Givens method (Reference 17) or a method due to Shavitt (Reference 18).

The matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$ may be reduced by appropriate operator algebra to the forms

$$H_{\mu\nu} = \sum_P \epsilon_P \left\langle \theta_M \left| \mathcal{O}_S P \right| \theta_M \right\rangle \left\langle \prod_{i=1}^n \Psi_{\mu i}(\underset{\sim}{r}_i, R) \left| \mathcal{H}(R) P \right| \prod_{i=1}^n \Psi_{\nu i}(\underset{\sim}{r}_i, R) \right\rangle \qquad (10)$$

$$S_{\mu\nu} = \sum_P \epsilon_P \left\langle \theta_M \left| \mathcal{O}_S P \right| \theta_M \right\rangle \left\langle \prod_{i=1}^n \Psi_{\mu i}(\underset{\sim}{r}_i, R) \left| P \right| \prod_{i=1}^n \Psi_{\nu i}(\underset{\sim}{r}_i, R) \right\rangle \qquad (11)$$

where P is a permutation and ϵ_p its parity. The sum is over all permutations. $\langle \theta_M | \mathcal{O}_S P | \theta_M \rangle$ is a "Sanibel coefficient" and the remaining factors are spatial integrals which can be factored into one- and two-electron integrals. If the $\phi_{\mu i}$ are orthonormal, Equations (10) and (11) become more tractable and the $H_{\mu\nu}$ and $S_{\mu\nu}$ may be evaluated by explicit methods given in the literature

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(Reference 15). Computer programs have been developed for carrying out this procedure, and they have been used for problems containing up to 106 total electrons, 10 unpaired electrons, and several thousand configurations.

The CI studies described above can be carried out for any orthonormal set of $\phi_{\mu i}$ for which the molecular integrals can be calculated. Programs developed by UTRC make specific provision for the choice of the $\phi_{\mu i}$ as Slater-type atomic orbitals, as symmetry molecular orbitals, as Hartree-Fock orbitals, or as more arbitrary combinations of atomic orbitals.

4. Molecular Integrals

The one- and two-electron integrals needed for the above described method of calculation are evaluated for STO's by methods developed by the present investigators (Reference 19). All needed computer programs have been developed and fully tested at UTRC.

5. Configuration Selection

Using a minimum basis plus polarization set of one-electron functions, a typical system can have of the order of 10^4 configurations in full CI (that resulting from all possible orbital occupancies). It is therefore essential to identify and use the configurations describing the significant part of the wavefunction. There are several ways to accomplish this objective. First, one may screen atomic-orbital occupancies to eliminate configurations with excessive numbers of anti-bonding orbitals. A third possibility is to carry out an initial screening of configurations, rejecting those whose diagonal energies and interaction matrix elements do not satisfy significance criteria. Programs to sort configurations on all the above criteria are available at UTRC.

Other, potentially more elegant methods of configuration choice involve formal approaches based on natural-orbital (Reference 20) or multiconfiguration SCF (Reference 21) concepts. To implement the natural-orbital approach, an initial limited-CI wavefunction is transformed to natural-orbital form, and the resulting natural orbitals are used to form a new CI. The hoped-for result is a concentration of the bulk of the CI wavefunction into a smaller number of significant terms. The multiconfiguration SCF approach is more cumbersome, but in principle more effective. It yields the optimum orbital choice for a preselected set of configurations. This approach works well when a small number of dominant configurations can be readily identified.

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It should be emphasized that the problem of configuration choice is not trivial, and represents an area of detailed study in this research. The existence of this problem causes integral evaluation to be far from a unique limiting factor in the work.

6. Density Function Approach – Xα Model

The Xα model (Reference 22) for the electronic structure of atoms, molecules, clusters and solids is a local potential model obtained by making a simple approximation to the exchange – correlation energy. If we assume a nonrelativistic Hamiltonian with only electrostatic interactions, it can be shown that the total energy E of a system can be written exactly (Reference 23) (in atomic units) as

$$E = \sum_i n_i < u_i \left| -\frac{1}{2} \nabla_i^2 + \sum_\mu \frac{z_\mu}{r_{i\mu}} \right| u_i > + \frac{1}{2} \sum_{\mu \neq \nu} \frac{z_\mu z_\nu}{r_{\mu\nu}}$$

$$+ \frac{1}{2} \sum_{ij} n_i n_j < u_i u_j \left| \frac{1}{r_{12}} \right| u_i u_j > + E_{xc} \qquad (12)$$

This expression is exact provided the u_i are natural orbitals and n_i are their occupation numbers (i.e., eigenfunctions and eigenvalues of the first order density matrix). The first term in Equation (12) represents the kinetic and electron-nuclear energies. The second term is the nuclear repulsion energy. The sums (μ, ν) are over all the nuclear charges in the system. The third term is the electron-electron repulsion term, which represents the classical electrostatic energy of the charge density ρ interacting with itself, where

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1) \qquad (13)$$

The last term E_{xc} represents the exchange correlation energy and can be expressed formally as

$$E_{xc} = \frac{1}{2} \int \rho(1) \, d\vec{r_1} \int \frac{\rho_{xc}(1,2)}{r_{12}} \, d\vec{r_2} , \qquad (14)$$

where $\rho_{xc}(1, 2)$ represents the exchange-correlation hole around an electron at position 1. In the exact expression, ρ_{xc} is dependent on the

second-order density matrix. In the Hartree-Fock approximation E_{xc} is the exchange energy, ρ_{xc} represents the Fermi hole due to the exclusion principle and depends only on the first-order density matrix. In the $X\alpha$ method, we make a simpler assumption about ρ_{xc}. If we assume that the exchange-correlation hole is centered on the electron and is spherically symmetric, it can be shown that the exchange-correlation potential

$$U_{xc} = \int \frac{\rho_{xc}(1,2)}{r_{12}} \; d\vec{r_2} \qquad (15)$$

is inversely proportional to the range of the hole, r_s, where r_s is defined by

$$\frac{4\pi}{3} \; r_s^3 \; \rho(1) = 1 \qquad (16)$$

Therefore, in the $X\alpha$ model, the potential U_{xc} is proportional to $\rho^{1/3}(\vec{r})$. We define a scaling parameter α such that

$$U_{x_\alpha}(1) = - \frac{9\alpha}{2} \; (3\rho(1)/8\pi)^{1/3} \qquad (17)$$

The expression in Equation (37) is defined so that $\alpha = 2/3$ for the case of a free electron gas in the Hartree-Fock model (Reference 24) and $\alpha = 1$ for the potential originally suggested by Slater (Reference 25). A convenient way to choose this parameter for molecular and solid state applications is to optimize the solutions to the $X\alpha$ equations in the atomic limit. Schwarz (Reference 26) has done this for atoms from $z = 1$ to $z = 41$ and found values between 2/3 and 1.

In the "spin polarized" version of the $X\alpha$ theory, it is assumed (as in the spin-unrestricted Hartree-Fock model) that electrons interact only with a potential determined by the charge density of the same spin. In this case the contribution to the total energy is summed over the two spins, $s = \pm 1/2$.

$$E_{xc} = \frac{1}{2} \sum_s \int \rho_s(1) \; U_{x\alpha,s}(1) d\vec{r_1} \qquad (18)$$

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where the potential is spin-dependent

$$U_{x_{\alpha,s}}(1) = -\frac{9\alpha}{2} \left(3\rho_s(1)/4\pi\right)^{1/3} \tag{19}$$

and ρ_s is the charge density corresponding to electrons of spin s. The spin polarized Xα model is useful for describing atoms and molecules with open-shell configurations and crystals which are ferromagnetic or anti-ferromagnetic.

Once one has made the Xα approximation to the total energy functional E in Equation (12), then the rest of the theory follows from the application of the variational principle. The orbitals u_i are determined by demanding that E be stationary with respect to variations in u_i. This leads to the set of one-electron Xα equations

$$\left[-\frac{1}{2}\nabla_1^2 + \sum_\mu \frac{z_\mu}{r_{1\mu}} + \int \frac{\rho(2)}{r_{12}}d\vec{r}_2 + \frac{2}{3}U_{x\alpha}\right] u_i = \epsilon_i u_i \tag{20}$$

where ϵ_i is the one-electron eigenvalue associated with u_i. Since $\rho(\vec{r})$ is defined in terms of the orbitals u_i, Equation (20) must be solved itera-tively, until self-consistency is achieved. Empirically, if one takes as an initial guess that ρ is approximately a sum of superimposed atomic charge densities, then the convergence of this procedure is fairly rapid. The factor of 2/3 multiplying the potential is a result of the linear dependence of E_{xc} on ρ. This also has a consequence that the Xα eigenvalues ϵ_i do not satisfy Koopman's theorem, i.e., they cannot be interpreted as ionization energies. However, it can be shown that the ϵ_i are partial derivatives of the total expression of Equation (12) with respect to the occupation number,

$$\epsilon_i = \frac{\partial E}{\partial n_i} \tag{21}$$

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If E were a linear function of n_i, then Koopmans' theorem would hold. However, because of the dominant Coulomb term, E is better approximated by a quadratic function in n_i. This leads to the "transition state" approximation which allows one to equate the difference in total energy between the state (n_i, n_j) and $(n_i - 1, n_j + 1)$ to the difference in the one-electron energies $\epsilon_j - \epsilon_i$ calculated in the state $(n_i - 1/2, n_j + 1/2)$. The error in this approximation is proportional to third-order derivatives of E with respect to n_i and n_j, which are usually small (Reference 27). The main advantage of using the transition state rather than directly comparing the total energy values is computational convenience, especially if the total energies are large numbers and the difference is small.

The relationship of Equation (21) also implies the existence of a "Fermi level" for the ground state. This can be seen by varying E with respect to n_i under the condition that the sum $\sum_i n_i$ is a constant, i.e.,

$$\delta \left[E - \lambda \sum_i n_i \right] = 0 \qquad (22)$$

implies $\partial E / \partial n_i = \lambda$, where λ is a Lagrangian multiplier. This implies that the total energy is stationary when all the one-electron energies are equal. However, the occupation numbers are also subject to the restriction $0 \leq n_i \leq 1$. This leads to the following conditions on the ground state occupation numbers;

$$\epsilon_i < \lambda \cdot) \cdot n_i = 1$$
$$\epsilon_i > \lambda \cdot) \cdot n_i = 0 \qquad (23)$$
$$\epsilon_i = \lambda \cdot) \cdot 0 \leq n_i \leq 1$$

In other words, the ground state eigenvalues obey Fermi statistics with λ representing the Fermi energy. It should be noted that, in contrast to the Hartree-Fock theory, where all the n_i are either 0 or 1, the Xα model predicts, in some cases, fractional occupation numbers at the Fermi level. In particular, this will occur in a system (such as transition metal or actinide atom) which has more than one open shell.

The Xα model differs in other significant ways from the Hartree-Fock method. In fact, the simplification introduced in approximating the total energy expression introduces several distinct advantages over Hartree-Fock:

1. The primary advantage is purely computational. The one-electron potential in Equation (20) is orbital-independent and local, i.e., it is the same for all electrons (except in the spin-polarized Xα theory) and is a multiplicative operator. On the other hand, the Hartree-Fock potential is nonlocal, or equivalently, there is a different local potential for each orbital. This involves a great deal more computational effort, especially for systems described by a large number of orbitals. It has been shown (Reference 28) that the Xα orbitals for the first and second row atoms are at least as accurate as a double-zeta basis set, and are probably better for larger atoms which involve electrons with $\ell \geq 2$.

2. The orbital-independent Xα potential leads to a better one-electron description of electronic excitations of a system. Both the unoccupied ($n_i = 0$) and occupied ($n_i = 1$) eigenfunctions are under the influence of the same potential resulting from the other N-1 electrons. The Hartree-Fock virtual orbitals see a potential characteristic of the N occupied orbitals, and therefore are not as suitable for describing the excited states. Actually, although the ground state virtual eigenvalues are usually a good description of the one-electron excitations, the virtual spectrum of the transition state potential where one-half an electron has been removed from the system gives a much better first-order picture of these levels (Reference 29).

3. As has been shown by Slater (Reference 30), the Xα model rigorously satisfies both the virtual and Hellman-Feynman theorems, independent of the value of the parameter α. This is convenient for calculating the force on a nucleus directly in terms of a three-dimensional integral, rather than the six-dimensional integrals in the expression for the total energy of Equation (12).

7. Computational Aspects of the Xα Method

In application of the Xα model to finite molecular systems, there are two practical aspects of the calculations which must be considered. The first

concerns the choice of the integration framework for describing the molecular wavefunctions and the second deals with the choice of the exchange parameter, α, in different regions of space.

In computations with heteronuclear molecules, there are several free parameters that must be chosen: the ratio of sphere radii for the atomic spheres of integration at a given internuclear separation, the degree of sphere overlap, and the value of the exchange parameter in the atomic spheres and the intersphere region.

It has been found that changing the ratio of the sphere radii for the two atoms in a heteronuclear diatomic molecule introduces changes in the total energy that can be large on a chemical scale (~ 1 eV). A choice for sphere radii based on covalent bonding radii does not necessarily provide a good estimate for these calculations. The value of the exchange parameter, α, and the sphere radii and/or sphere overlap is normally fixed in $X\alpha$ calculations for crystals where the geometry is fixed. However, to develop a potential curve, the molecule description needs to change substantially as the internuclear separation varies and the changing sphere radii include varying fractions of the total molecular charge (Reference 31). Studies made at UTRC have shown that at any given separation the total energy calculated from the $X\alpha$ model is a minimum at the radii ratio where the spherically averaged potentials from the two atomic centers is equal at the sphere radius.

$$V_1(r_{s_1}) = V_2(r_{s_2}) \tag{24}$$

This relationship between the potential match at the sphere boundary and the minimum in the total energy appears to hold exactly for "neutral" atoms and holds well for ionic molecular constituents. In the case of two ionic species, the long range tail of the potential must go like $+2/R$ from one ion and $-2/R$ (in Rydbergs) for the other ion and so at large internuclear separations, the tails of the potential cannot match well. However, at reasonable separations, the $1/R$ character of the potential does not invalidate the potential match criterion for radii selection. This match for the atomic potentials is applied to the self-consistent potentials.

In molecules with significant charge sharing in the bonds, the radii of the atomic spheres is frequently increased in Xα calculations so that an over-lap region appears in the vicinity of the bond (Reference 32). Studies made at UTRC show that the contribution to the total molecular energy from the exchange integral shows a minimum at the optimum sphere radius or sphere over-lap. This provides a sensitive criterion for selecting these parameters.

The values of the exchange parameters in the spherical integration region around each atomic center are frequently set at the atomic values both for neutral and for ionic molecular constituents. However, for light atoms, the value of α which best reproduces Hartree-Fock results varies substantially with ionicity. In argon, the following table compares, for the neutral atom and the positive ion, the HF energy and the Xα energy calculated for several values of α.

	α	Xα Energy	HF Energy
Ar^0	.72177	526.8176	526.8173
$Ar^{+1/2}$	.72177	526.5857	–
	.72213	526.6007	–
Ar^{+1}	.72177	526.2447	–
	.72213	526.2596	–
	.72249	526.2745	526.2743

The optimum value of α changes even more rapidly in the fluorine atom going from 0.73732 for F^0 to .72991 for F^{-1}. Since the total energy depends linear-ly on α, this parameter must be chosen carefully.

The intersphere exchange coefficient is chosen to be a weighted average of the atomic exchange parameters from the two constituents. At small inter-nuclear separations, the optimum radius for an atomic sphere frequently places significant amounts of charge outside that atomic sphere – charge that is still strongly associated with its original center rather than being trans-ferred to the other center or associated with the molecular binding region. To best account for these cases the weighting coefficients are chosen to reflect the origin of the charge in the intersphere (or outersphere region),

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$$\alpha_{\text{intersphere}} = \frac{\alpha_{s_1}(Q_{s_1} - Q_1^{\,o}) + \alpha_{s_2}(Q_{s_2} - Q_2^{\,o})}{(Q_{s_1} - Q_1^{\,o}) + (Q_{s_2} - Q_2^{\,o})} \qquad (25)$$

where $(Q_{s_i} - Q_i^{\,o})$ is the charge lost from sphere i relative to its atomic value (or ionic value) $Q_i^{\,o}$ and α_{s_i} is the atomic exchange parameter for sphere i. This value for $\alpha_{\text{intersphere}}$ is calculated dynamically - it is updated after each iteration in the self-consistent calculation.

While for heavy atoms, these changes in the exchange parameter would be small, the α's for small atoms vary rapidly with z (and with ionicity). The correct choice of the exchange parameters influences not only the total energy calculated for the molecule but also in some cases affects the distribution of charge between the atomic spheres and the intersphere region.

B. TRANSITION PROBABILITIES

The electronic and vibrational-rotational wavefunctions of a pair of states can be used to calculate transition probabilities. If two molecular states are separated in energy by an amount $\Delta E_{nm} = hc\nu$ (h = Planck's constant, c = velocity of light, ν = frequency in wave numbers), the semi-classical theory of radiation (References 90 and 91) yields for the probability of a spontaneous transition from an upper state n to a lower state m

$$A_{nm} = \frac{4}{3} \frac{\Delta E_{nm}^3}{\hbar^4 c^3} \frac{S_{nm}}{g_n} \tag{26}$$

Here A_{nm} is the Einstein coefficient for spontaneous transition from level n → m, g_n is the total degeneracy factor for the upper state

$$g_n = (2 - \delta_{\sigma, \Lambda'})(2S' + 1)(2J' + 1) \tag{27}$$

and S_{nm} is the total strength of a component line in a specific state of polarization and propagated in a fixed direction. A related quantity is the mean radiative lifetime of state n defined by

$$\frac{1}{\tau_n} = \sum_{m<n} A_{nm} \tag{28}$$

the summation being over all lower levels which offer allowed connections. The intensity of the emitted radiation is

$$I_{nm} = \Delta E_{nm} N_n A_{nm} \tag{29}$$

where N_n is the number density in the upper state n. This analysis assumes that all degenerate states at the same level n are equally populated, which will be true for isotropic excitation. The total line strength S_{nm} can be written as the square of the transition moment summed over all degenerate components of the molecular states n and m:

$$S_{nm} = \sum_{i,j} \left| M_{ji} \right|^2 \qquad (30)$$

where j and i refer to all quantum numbers associated collectively with upper and lower electronic states, respectively.

In the Born-Oppenheimer approximation, assuming the separability of electronic and nuclear motion, the wavefunction for a diatomic molecule can be written as

$$\psi'_{vJM\Lambda} = \psi'_{el}(\underline{r}, R)\, \psi_v(R)\, \psi_{JM\Lambda}(\theta, \chi, \phi) \qquad (31)$$

where $\psi^i_{el}(\underline{r}, R)$ is an electronic wavefunction for state i at fixed internuclear separation R, $\psi_v(R)$ is a vibrational wvefunction for level v and $\psi_{Jn\Lambda}(\theta, x, \phi)$ refers to the rotational state specified by electronic angular momentum Λ, total angular momentum J and magnetic quantum number M. The representation is in a coordinate system related to a space-fixed system by the Eulerian angles (θ, x, ϕ). The transition moment M_{ji} can be written, using the wavefunction given by Equation (31), as

$$M_{ji} = \int \psi^j_{v'J'\Lambda'M'} \left\{ \underline{M}^e + \underline{M}^n \right\} \psi^j_{v''J''\Lambda''M''}\, d\tau_e\, d\tau_v\, d\tau_r \qquad (32)$$

The subscripts e, v and r refer to the electronic, vibrational and rotational wavefunctions and $\underline{M}^e$ and $\underline{M}^n$ are the electronic and nuclear electric dipole moments, respectively. Integration over the electronic wavefunction, in the Born-Oppenheimer approximation, causes the contribution of the nuclear moment M^n to vanish for $i \neq j$. The electronic dipole moment can be written (References 91 and 92) in the form

$$\underset{\sim}{M}^e = -\sum_k e\underset{\sim}{r}_k' = -\left\{\sum_k e\underset{\sim}{r}_k\right\}\cdot\underset{\sim}{\mathfrak{D}}(\theta,\chi,\phi) \tag{33}$$

where the primed coordinates refer to the space fixed system, the coordinates r_k refer to a molecule-fixed system and $\underset{\sim}{\mathfrak{D}}(\theta, \chi, \phi)$ is a group rotation tensor whose elements are the direction cosines related to the Eulerian rotation angles (θ, χ, ϕ). Using bracket notation, Equations (32) and (33) can be combined to yield for the transition moment

$$M_{ji} = M_{iv''J''\Lambda''M''}^{jv'J'\Lambda'M'} = \left\langle jv'\left|-\sum_k e\underset{\sim}{r}_k\right|iv''\right\rangle\cdot\left\langle J'\Lambda'M'\left|\underset{\sim}{\mathfrak{D}}(\theta,\chi,\phi)\right|J''\Lambda''M''\right\rangle \tag{34}$$

The matrix elements $\langle J'\ \Lambda'\ M'|\ (\theta, \chi, \phi)|J''\ \Lambda''\ M''\rangle$ determine the group selection rules for an allowed transition and have been evaluated for many types of transitions (References 36-38). Summing Equation (34) over the degenerate magnetic quantum numbers M' and M'' we have from Equation (30)

$$S_{nm} = S_{mv''J''\Lambda''}^{nv'J'\Lambda'} = \mathscr{S}_{J''\Lambda''}^{J'\Lambda'}\ p_{mv''}^{nv'} \tag{35}$$

where $\overset{..}{\mathstrut}_{J''\Lambda''}^{J'\Lambda'}$ is the Hönl-London factor (References 39 and 40)

$$\wp_{mv''}^{nv'} = \sum_{i,j}\left|\left\langle jv'\left|-\sum_k e\underset{\sim}{r}_k\right|iv''\right\rangle\right|^2 \tag{36}$$

is the band strength for the transition. Combining Equations (27), (29) and (35), we have for the intensity of a single emitting line from upper level n:

$$I_{nm} = I_{mv''J''}^{nv'J'} = \frac{4}{3}\ N_{J'}\ \frac{\left[\Delta E_{mv''J''}^{nv'J'}\right]^4 S_{mv''J''\Lambda''}^{nv'J'\Lambda'}}{\hbar^4 c^3\omega_n(2J'+1)} \tag{37}$$

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where N_J'' is the number density in the upper rotational state J' and $\omega_n = (2-\delta_{\sigma,\Lambda})(2S'+1)$ is the electronic degeneracy. Taking an average value of $E_m^{n\ v'J'}{}_{v''J''}$ for the whole band, Equation (37) can be summed to yield the total intensity in the (v', v'') band:

$$I_{mv''}^{nv'} = \sum_{J',J''} I_{mv''J''}^{nv'J'} = \frac{4}{3} N_{v}' \frac{\left[\overline{\Delta E}_{mv''}^{nv'}\right]^4 p_{mv''}^{nv'}}{\hbar^4 c^3 \omega_n} \tag{38}$$

where $N_{v'} = \sum_{J'} N_{j'}$ is the total number density in the upper vibrational level v' and where we make use of the group summation property

$$\sum_{J''} \mathcal{S}_{J''\Lambda''}^{J'\Lambda'} = (2J'+1) \tag{39}$$

Comparing Equations (29) and (38), we have for the Einstein spontaneous transition coefficient of the band (v', v'')

$$A_{mv''}^{nv'} = \frac{4}{3} \frac{\left[\Delta E_{mv''}^{nv'}\right]^3 p_{mv''}^{nv'}}{\hbar^4 c^3 \omega_n} \tag{40}$$

Similarly, the lifetime of an upper vibrational level v' of state n can be written

$$\frac{1}{\tau_n} = \sum_{m<n} \sum_{v''} A_{mv''}^{nv'} \tag{41}$$

where the summation runs over all v'' for each lower state m. Equation (40) can be cast in the computational form

$$A_{mv''}^{nv'} (\sec^{-1}) = \frac{(21.41759 \times 10^9)}{\omega_n} \left[\Delta E_{mv''}^{nv'} (a.u.)\right]^3 p_{mv''}^{nv'} (a.u.) \tag{42}$$

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where $\Delta E_{m\,v''}^{n\,v'}$ and $p_{m\,v''}^{n\,v'}$ are in atomic units. It is also often convenient to relate the transition probability to the number of dispersion electrons needed to explain the emission strength classically. This number, the f-number or oscillator strength for emission, is given by

$$f_{nm,\,v'v''} = \frac{mc^3 h^2}{2e^2 \left[\overline{\Delta E}_{m\,v''}^{n\,v'}\right]^2} \, A_{m\,v''}^{n\,v'} \tag{43}$$

The inverse process of absorption is related to the above development through the Einstein B coefficient. Corresponding to Equation (29), we have for a single line in absorption

$$\frac{I_{m\,v''}^{n\,v'}}{I_\nu^0 \Delta x} = \int_{\text{line}(v''v'J''J')} K(\nu)\,d\nu = \overline{\Delta E}_{mn} N_m B_{mn} \tag{44}$$

where $K(\nu)$ is the absorption coefficient of a beam of photons of frequency ν and

$$B_{mn} = B_{m v''J''\Lambda''}^{n v'J'\Lambda'} = \frac{2\pi}{3\hbar^2 c} \, \frac{S_{m v''J''\Lambda''}^{n v'J'\Lambda'}}{\omega_m (2J''+1)} \tag{45}$$

is the Einstein absorption coefficient for a single line. Summing over all lines in the band (v'', v'), assuming an average band frequency, we obtain

$$\frac{I_{m\,v''}^{n\,v'}}{I_v^0 \Delta x} = N_{v''} \frac{2\pi}{3\hbar^2 c\,\omega_m} \, p_{m v''}^{n v'} \, \Delta \overline{E}_{m v''}^{n v'} \tag{46}$$

where $N_{v''} = \sum_{J''} N_{J''}$ is the total number density in the lower vibrational state v''. Corresponding to Equations (42) and (43) we can define an f-number or oscillator strength for absorption as

$$f_{mn,v''v'} = \frac{2m \, \overline{\Delta E}_{mv''}^{nv'}}{3\hbar^2 e^2 \omega_m} \, p_{mv''}^{nv'} \tag{47}$$

In computational form, Equation (47) becomes

$$f_{mn,v''v'} = \frac{2}{3} \cdot \frac{\overline{\Delta E}_{mv''}^{nv'}(a.u.)}{\omega_m} \, p_{mv''}^{nv'} \, (a.u.) \tag{48}$$

where $\overline{\Delta E}_{m \, v''}^{n \, v'}$ and $p_{m \, v''}^{n \, v'}$ are in atomic units. Combining Equations (40) and (43) and comparing with Equation (47), we see that the absorption and emission f-numbers are related by

$$f_{mn,v''v'} = \left(\frac{\omega_n}{\omega_m}\right) f_{nm,v'v''} \tag{49}$$

Some caution must be observed in the use of f-numbers given either by Equation (43) or (47) since both band f-numbers and system f-numbers are defined in the literature. The confusion arises from the several possible band averaging schemes that can be identified.

An integrated absorption coefficient (density corrected) can be defined from Equation (46) as

$$S_{v'',v'} = \frac{1}{P_c} \, I_{mv''}^{nv'} = N_{v''} B_{v'',v'} \left(1 - \exp\frac{-hc\nu_{v'',v'}}{kT}\right) \frac{h\nu_{v''v'}}{Pc^2} \tag{50}$$

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where the exponential factor corrects for stimulated emission. Equation 50 can be written in terms of the absorption f-number as

$$S_{v'',v'} = \frac{\pi e^2}{mc^2} \frac{N_{v''}}{P} \left(1 - \exp \frac{-hc\nu_{v'',v'}}{kT} \right) f_{mn,v''v'} \tag{51}$$

Using $h\,c/k = 1.43880$ cm-K°, we obtain a computational formula for the integrated absorption coefficient as $S_{v'',v'}$ $(cm^{-2} \cdot atm^{-1}) =$

$$2.3795 \times 10^7 \left(\frac{273.16}{T(K^\circ)} \right) \left(\frac{N_{v''}}{N_T} \right) \left(1 - \exp \frac{-1.43880\,\nu_{v'',v'}\,(cm^{-1})}{T(K^\circ)} \right) f_{mn,v''v'} \tag{52}$$

The total integrated absorption is found from

$$S_{TOTAL} = \sum_{v''} \sum_{v'} S_{v'',v'} \tag{53}$$

where, under normal temperature conditions, only the first few fundamentals and overtones contribute to the summations.

The developments given above are rigorous for band systems where an average band frequency can be meaningfully defined. Further approximations, however, are often made. For example, the electronic component of the dipole transition moment can be defined as

$$R_{ji}(R) = \left\langle j \left| -\sum_k e\underset{\sim}{r}_k \right| i \right\rangle \tag{54}$$

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This quantity is often a slowly varying function of R and an average value can sometimes be chosen. Equation (36) can then be written approximately in factored form as

$$\mathcal{P}_{mv''}^{nv'} \simeq q_{v'v''} \sum_{i,j} \left| \bar{\mathcal{R}}_{ji}(\bar{R}) \right|^2 \tag{55}$$

where $q_{v'v''}$, the square of the vibrational overlap integral, is called the Franck-Condon factor. $\mathcal{R}_{ji}$ is evaluated at some mean value of the internuclear separation R. In addition, it is sometimes possible to account for a weak R-dependence in $\underset{\sim}{M}^e$ by a Taylor series expansion of this quantity about some reference value, $\mathcal{R}_{\alpha\beta}$, usually referred to the (0, 0) band. We have

$$\mathcal{R}_{ji} \simeq \mathcal{R}_{ji}^{\alpha\beta} \left[1 + a(R - R_{\alpha\beta}) + b(R - R_{\alpha\beta})^2 + \cdots \right] \tag{56}$$

Substituting into Equation (56) and integrating yields

$$\mathcal{P}_{mv''}^{nv'} \simeq q_{v'v''} \sum_{i,j} \left| \mathcal{R}_{ji}^{\alpha\beta} \left[1 + a(\overline{R_{v'v''} - R_{\alpha\beta}}) + b(\overline{R_{v'v''} - R_{\alpha\beta}})^2 + \cdots \right] \right|^2 \tag{57}$$

where

$$(\overline{R_{v'v''} - R_{\alpha\beta}}) = \frac{\left\langle v' \left| (R - R_{\alpha\beta}) \right| v'' \right\rangle}{\left\langle v' \mid v'' \right\rangle} \tag{58}$$

is the R-centroid for the transition and

$$(\overline{R_{v'v''} - R_{\alpha\beta}})^2 = \frac{\left\langle v' \left| (R - R_{\alpha\beta})^2 \right| v'' \right\rangle}{\left\langle v' \mid v'' \right\rangle} \tag{59}$$

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is the R^2-centroid. Note that this last term differs (to second order) from the square of the R-centroid. An alternate procedure can be developed by evaluating Equation (54) at each R-centroid, $\overline{R}_{v'v''}$. Then

$$p_{mv''}^{nv'} \approx q_{v'v''} \sum_{i,j} |R_{ji}(R_{v'v''})|^2 \tag{60}$$

Equation (60) assumes that the vibrational wavefunction product $\psi_{v'} \psi_{v''}$, behaves like a delta function upon integration,

$$\psi_{v'} \psi_{v''} = \delta(R - \overline{R}_{v'v''}) \langle v'|v'' \rangle \tag{61}$$

The range of validity of Equation (60) is therefore questionable, particularly for band systems with bad overlap conditions such as oxygen Schumann-Runge. The range of validity of the R-centroid approximation has been examined by Frazer (Reference 41).

The final step in calculating transition probabilities is the determination of $R_{ji}(R)$, the electronic dipole transition moment, for the entire range of internuclear separations, R, reached in the vibrational levels to be considered. This can be expressed in terms of the expansion of Equation (4) as

$$R_{ji}(R) = \sum_{\mu\nu} c_\mu^{j*} c_\nu^i \langle \psi_\mu(R)| \underset{\sim}{M}^e |\psi_\nu(R) \rangle \tag{62}$$

where c_μ^j and c_ν^i are coefficients for ψ_{el}^j and ψ_{el}^i, respectively.

An analysis similar to that yielding Equation (10) and (11) gives

$$\langle \psi_\mu(R) | \underset{\sim}{M}^e | \psi_\nu(R) \rangle =$$

$$\sum_p \epsilon_p \langle \theta_{M_S} | \mathcal{O}_S P | \theta_{M_S} \rangle \langle \prod_{k=1}^{n} \psi_{\mu k}(\underset{\sim}{r}_k, R) | \underset{\sim}{M}^e P | \prod_{k=1}^{n} \psi_{\nu k}(\underset{\sim}{r}_k, R) \rangle$$

The spatial integral in Equation (63) reduces to one-electron integrals equivalent to overlap integrals, and the evaluation of Equation (63) can be carried out by the same computer programs used for Equation (11). Programs for evaluating $R_{ji}(R)$ in Equation (62) have been developed at UTRC and examples of their application have appeared in the literature (Reference 8).

For perturbed electronic systems, the transition dipole moment will have a strong R-dependence and R-centroid or other apporximations will be invalid. A direct evaluation of Equation (36) would therefore be required using the fully-coupled system of electronic and vibrational wavefunctions to properly account for the source of the band perturbations.

SECTION 3

DISCUSSION OF RELATIVISTIC METHODS

For heavy atoms ($Z \gtrsim 30$), and molecular systems built from heavy atoms, relativistic effects become increasingly important and should be taken into account in the calculation of the radial wavefunctions. The implementation of relativistic effects into atomic and molecular computer codes is only fairly recent owing to the increased complexities introduced in the self-consistent field (SCF) procedure and the greatly increased computer time required for such calculations. Compared with the non-relativistic case, the Dirac-Hartree-Fock (DHF) method requires that two radial functions, G_{nlj}, corresponding to the large component and F_{nlj}, corresponding to the small component must be calculated for each of the two possible j values. Thus, the numerical work of a DHF relativistic treatment is increased by nearly a factor of four over the nonrelativistic case, exclusive of increased complexities in evaluation of the terms of the Hamiltonian. In view of this, methods that have been developed to date for molecular systems have involved the use of model potentials to represent relativistic effects.

In the calculation of the internal energy of a molecular system comprised of n electrons and N nuclei, and considering only electrostatic interactions between the particles, we have for the total Hamiltonian

$$\mathcal{H} = \mathcal{H}_{el} - \sum \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 + \frac{\hbar^2}{2M_T} \left[\sum_{\substack{\beta=1 \\ \alpha \neq \beta}}^{N} \sum_{\alpha=1}^{N} \nabla_\alpha \cdot \nabla_\beta \right. \tag{64}$$

where

$$\left. + 2 \sum_{\alpha=1}^{N} \sum_{i=1}^{n} \nabla_\alpha \cdot \nabla_i + \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j}}^{n} \nabla_i \cdot \nabla_j \right]$$

$$\mathcal{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 + V^{el}(r_n, R_N) \tag{65}$$

where m_e, m_α, M_T, are the masses of the electron, atom α and combined system mass, respectively. Now since the ratios m_e/m_α and m_e/M_T are both small,

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$(2 \times 10^{-6} - 5 \times 10^{-4})$ we can effect a separation of the electronic and nuclear coordinates treating the total wavefunction as a product of a nuclear and an electronic part. We have

$$\psi(\underset{\sim}{r}_n, \underset{\sim}{R}_N) = \sum_k \chi_k(\underset{\sim}{R}_N) \, \psi_k(\underset{\sim}{r}_n, \underset{\sim}{R}_N) \tag{66}$$

where $\psi_k(\underset{\sim}{r}_n, R_N)$ is an electronic wavefunction parametric in the nuclear coordinates as given in Equation (66) and $\chi_k(\underset{\sim}{R}_N)$ are nuclear motion wavefunctions which satisfy (neglecting terms of the order of m_e/m_α)

$$\left[-\sum_{\alpha=1}^N \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 + \frac{\hbar^2}{2M_T} \sum_{\substack{\alpha=1 \\ \alpha \neq \beta}}^N \sum_{\beta=1}^N \nabla_\alpha \cdot \nabla_\beta + V^{el}(\underset{\sim}{r}_n, \underset{\sim}{R}_N) \right] \chi_k = i\hbar \frac{\partial \chi_k}{\partial t} \tag{67}$$

The cross term in $\nabla_\alpha \cdot \nabla_\beta$ can be eliminated by a proper change of variables and Equation (67) then reduces to a 3N-3 dimensional Schrödinger equation.

For most systems, where the velocity of motion of the nuclei is slow relative to the electron velocity, this decoupling of electronic and nuclear motion is valid and is referred to as the adiabatic approximation. Equation (66) thus defines an electronic eigenstate $\psi_k(\underset{\sim}{r}_n, \underset{\sim}{R}_N)$, parametric in the nuclear coordinates, and a corresponding eigenvalue $E_k(\underset{\sim}{R}_N)$ which is taken to represent the potential energy curve or surface corresponding to state k.

In the usual ab initio method for calculating the electronic properties of a molecular system, one starts from a zero-order Hamiltonian that is exact except for relativistic and magnetic effects, and which involves the evaluation of electronic energies and other relevant quantities for wavefunctions that are properly antisymmetrized in the coordinates of all the electrons. For a system containing n electrons and M nuclei, the zero-order Hamiltonian depends parametrically on the nuclear positions and is of the form

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$$\mathscr{H}_e = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{j=1}^{M}\frac{z_j}{\left|\vec{r}_i - \vec{R}_j\right|} + \sum_{1\leq i<j}^{M}\frac{z_i\,z_j}{\left|\vec{R}_i - \vec{R}_j\right|} + \sum_{1\leq i<j}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} \qquad (68)$$

where z_i and $\vec{R}_i$ are the charge and position of nucleus i, $\vec{r}_j$ is the position of electron j, and ∇_j^2 is the Laplacian operator for electron j. All quantities are in atomic units, i.e. lengths in bohrs, energies in hartrees (1 hartree = 2 Rydbergs).

In addition to the electrostatic contribution, $\mathscr{H}_e$, the complete Hamiltonian should contain additional terms which correct for magnetic interactions and relativisitic effects. These correction terms may be of importance in several applications. These include:

(1) calculation of the probability of making a transition from one quantum state to another in high-momentum collisions such as those that can occur in hot atom or heavy atom chemical dynamics experiments;

(2) determination of the interaction energy in heavy nuclei systems such as Cs_2 and UO^+, which exhibit open-shell structure on both nuclei at infinite internuclear separations;

(3) calculation of the intermolecular forces between free radicals, electronically excited states of molecules with open-shell structure, and long molecular conformations of possible biological interest.

A. BREIT-PAULI HAMILTONIAN

The relativistic correction terms to the usual electrostatic Hamiltonian have been derived through order α^2, where α is the fine structure constant, and are often referred to as the Breit-Pauli (Reference 42) Hamiltonian terms. This Hamiltonian has been derived by Bethe and Salpeter (Reference 43) for a two-electron system and has been generalized to the many-electron system by Hirschfelder, et al (Reference 44) and Itoh (Reference 45). In the absence of external electric or magnetic fields we can represent these correction terms as follows. Let $\vec{s}_j$ and $\vec{p}_j = \frac{1}{i}\Delta_j$ denote the operators for the spin and linear

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moment of electron j, respectively. Then the generalized Breit-Pauli Hamiltonian, correct to terms of $\mathcal{O}(\alpha^2/M)$, can be written as:

$$\mathcal{H}_{BP} = \mathcal{H}_e + \mathcal{H}_{LL} + \mathcal{H}_{SS} + \mathcal{H}_{LS} + \mathcal{H}_p + \mathcal{H}_D \tag{69}$$

where $\mathcal{H}_e$ is given by Equation (68) and the correction terms can be expressed as follows:

$$\mathcal{H}_{LL} = -\frac{1}{2} \sum_{1 \le k \le j} \frac{1}{r_{jk}^3} \left[r_{jk}^2 \; \vec{p}_j \cdot \vec{p}_k + \vec{r}_{jk} \cdot (\vec{r}_{jk} \cdot \vec{p}_j) \, p_k \right] \tag{70}$$

$$\mathcal{H}_{SS} = \sum_{1 \le k < j} \left\{ -\left(\frac{8\pi}{3}\right) \vec{s}_j \cdot \vec{s}_k \; \delta(\vec{r}_{jk}) \right.$$
$$\left. + \frac{1}{r_{jk}^5} \left[r_{jk}^2 \; (\vec{s}_j \cdot \vec{s}_k) - 3 (\vec{s}_j \cdot \vec{r}_{jk})(\vec{s}_k \cdot \vec{r}_{jk}) \right] \right. \tag{71}$$

$$\mathcal{H}_{LS} = \frac{1}{2} \sum_{\alpha} \sum_{j} \left(\frac{z_\alpha}{r_{j\alpha}^3}\right) (\vec{r}_{j\alpha} \cdot \vec{p}_j) \cdot \vec{s}_j$$
$$- \frac{1}{2} \sum_{1 \le k \le j} \frac{1}{r_{jk}^3} \left[(\vec{r}_{jk} \times \vec{p}_j) \cdot \vec{s}_j - 2 (\vec{r}_{jk} \times \vec{p}_k) \cdot \vec{s}_j \right] \tag{72}$$

$$\mathcal{H}_p = -\frac{1}{8} \sum_{j} p_j^4 \tag{73}$$

$$\mathcal{H}_D = \frac{\pi}{2} \left[\sum_{\alpha} \sum_{j} z_\alpha \, \delta(\vec{r}_{j\alpha}) - 2 \sum_{1 \le k < j} \delta(\vec{r}_{jk}) \right] \tag{74}$$

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The first correction term $\mathcal{H}_{LL}$, represents the magnetic orbit-orbit coupling terms of the electrons arising from the interaction of the magnetic fields created by their motion. The second term, $\mathcal{H}_{SS}$, gives the spin-spin magnetic coupling terms which are often quite appreciable. For $r_{jk} = 0$, only the delta-function contribution survives which represents the Fermi-contact spin interaction. The third term, $\mathcal{H}_{LS}$, is usually the largest in magnitude and represents the spin-orbit interaction between the spin and magnetic moment of each electron and the spin-other orbit interaction, which represents the coupling of the spin of one electron with the magnetic moment of a different electron. The term, $\mathcal{H}_p$, corrects for variation of the electron mass with velocity and the term, $\mathcal{H}_D$, represents electron spin terms identified by Dirac which appear to have no classical analogue.

Aside from the spin-orbit term, $\mathcal{H}_{LS}$, usually only the last term, $\mathcal{H}_D$, (often called the Darwin correction term) and $\mathcal{H}_p$, the mass-velocity term, are retained in the Hamiltonian, yielding the so-called Pauli approximation (Reference 43).

The eigenfunctions of the Hamiltonian represented by Equation (69) are four-component Dirac spinors which may be expressed as:

$$r \, \psi_{nkm} = \begin{pmatrix} P_{nk}(r) \; \chi_{km}(\theta,\phi) \\ i Q_{nk}(r) \; \chi_{-km}(\theta,\phi) \end{pmatrix} \tag{75}$$

where $\chi_{km}(\theta, \phi)$ are products of spherical harmonics and Pauli spinors and $P_{nk}(r)$, $Q_{nk}(r)$ represent, respectively, the large and small components of the radial wave equation. The exact solution of the Breit-Pauli Hamiltonian has only been given for one- and two-electron atomic systems (Reference 43) owing to the complexity of the operators for the general n-electron case. For a molecular system, Kolos and Wolniewicz (Reference 46) have calculated the relativistic corrections to H_2 using Equation (69) to $\mathcal{O}(\alpha^2)$. No heavier molecular systems have been treated using the full Breit-Pauli Hamiltonian.

B. APPROXIMATE TREATMENTS

Although the Breit-Pauli Hamiltonian given in Equation (69) can formally be employed in a molecular system, both the multiplicity of terms and the difficulty of evaluation of the resultant molecular integrals has precluded its general use to date. For atomic systems, various approximate methods of solution, within a Hartree-Fock or multiconfiguration Hartree-Fock framework, have been proposed for atoms (References 47-51). In most of these methods, a restricted Hamiltonian which includes only the one-electron Dirac terms is usually employed. The contributions of the Breit operators for spin-magnetic interactions and velocity retardation are then calculated as first-order perturbations using the zeroth-order Dirac relativistic wavefunctions.

An even more approximate method for incorporating the major relativistic effects has been proposed by Cowan and Griffin (Reference 52). In this method, the mass-velocity $(\mathcal{H}_p)$ and Darwin $(\mathcal{H}_D)$ terms, written in terms of the Pauli equation for one-electron atoms, are simply added to the usual non-relativistic Hamiltonian operator. In addition, the spin-orbit terms, $\mathcal{H}_{LS}$, are omitted, thereby reducing the system of equations to a single form representing the description of the major component wavefunction, $P_{nk}(r)$, evaluated at the center-of-gravity of the spin-orbit states. The rationale for this approximation lies in the observation that detailed atomic calculations using the complete DHF method have indicated that, even for an atom as heavy as uranium, less than 1 percent of the total charge is described by the small component radial wavefunctions.

The resulting equations have the form:

$$\left[-\frac{d^2}{dr^2} + \frac{\ell_i(\ell_i+1)}{r^2} + V^i(r) + H_m^i(r) + H_D^i(r) \right] G_{n\ell}^i(r) = \epsilon_{n\ell}^i \, G_{n\ell}^i(r) \tag{76}$$

where the mass-velocity and Darwin terms take the form

$$H^i_m (r) = - \frac{\alpha^2}{4} \left[\epsilon^i - v^i (r) \right]^2 \tag{77}$$

$$H^i_D (r) = - \delta_{\ell_i,0} \; \frac{\alpha^2}{4} \left[1 + \frac{\alpha^2}{4} (\epsilon^i - v^i (r)) \right]^{-1} \left[\frac{dv^i(r)}{dr} \left(\frac{d}{dr} - \frac{1}{r} \right) \right] \tag{78}$$

and $\alpha \sim 1/137.036$ is the fine structure constant. The spin-orbit term is omitted in Equation (76) and thus these equations represent center of gravity radial functions averaged over the two possible total angular momentum quantum numbers. Equation (76) represents (apart from the neglect of spin-orbit effects) the relativistic corrections to first order in α^2. A more accurate analysis of heavy atom energy levels and spectra is available through the use of the radial functions, $G^i_{nl}(r)$, found from Equation (76), and a first-order perturbation calculation. Cowan and Griffin (Reference 52) have illustrated the utility and accuracy of such an approach.

Recently, Wood and Boring (Reference 53) have adapted this approximate relativistic method to the local exchange problem and have implemented the solution of Equation (76) within the context of the multiple scattering Xα method (Reference 22). The central field Hamiltonian is modified to include mass-velocity and Darwin terms, given by Equations (77) and (78), in the sphere surrounding each atomic center. The intersphere region in the multiple scattering approach (constant potential region) is treated nonrelativistically since charge in this region is far from a nucleus and is screened by the charge concentrated around the atomic centers. The matching conditions for continuity of the wavefunction at the sphere boundaries permits any necessary charge transfer between the relativistic intra-atomic regions and the nonrelativistic interatomic constant potential regions. For an atom, the Wood-Boring treatment reduces to the Dirac-Slater local exchange method, but with the neglect of spin-orbit terms.

The implementation of Equation (76) into existing nonrelativistic multiple scattering molecular codes is facilitated by a change in the dependent variable, $G^i_{nl}(r)$, to eliminate the first derivative of the wavefunction, illustrated in Equation (78). The usual Numerov method of solution can then be applied to the central field problem; the only new requirement being the numerical tabulation of the first and second derivatives of the potential at each grid point in the integrations. These derivatives are computed only once for each complete SCF cycle and thus the total required computer time for a typical problem is not significantly increased as compared with a nonrelativistic calculation. A complete self-consistent program incorporating this method has been developed at UTRC. Our code has been tested by repeating calculations for the U and Pu atoms (Reference 52), where we find excellent agreement with the more exact, but cumbersome, Dirac-Slater calculations. Results for molecular calculations have recently been reported by Boring and Wood for UF_6 and UO_2^{++} (References 54 and 55). These calculations were carried out to illustrate the shifts in the valence levels for such systems resulting from relativistic effects. The total energy was not of principal concern.

We have recently reported (Reference 56) the first all-electron calculation of the potential energy curves for a molecule (Hg_2^+) built from atoms which exhibit significant relativistic effects. This study illustrated that reliable total energies are obtainable through a relativistic multiple scattering density functional treatment, provided care is taken to optimize potential match and overlap criteria for such systems. This study formed the basis of the computational scheme that we have employed here for the uranium/oxygen system.

C. EFFECTIVE CORE MODELS

It is well known from chemical experience that the outermost valence electrons contribute most to determining the chemical properties, especially spectroscopic properties, of molecules. The core electrons remain essentially unchanged from their atomic form except for internuclear separations of the order of the charge radii of the outer core region or less, wherein core polarization effects may become important. Since the computational time

required for ab initio calculations of electronic structure goes up at least quadratically with the number of electrons in the system, there have been many attempts to replace the more tightly bound core electrons with simple one-electron effective potentials (References 57-65). Concurrent with elimination of an explicit treatment of the core electrons, a transformation of the valence orbital basis is required to insure that the lowest valence orbital of each symmetry has a nodeless radial form, since it is well known that the lowest energy eigenfunction for a local potential must be nodeless (Reference 66).

Typical of the several effective core models that have been reported is that due to Kahn, et al (Reference 64) whereby an effective core potential is described in terms of angularly dependent projection operators as

$$U^{core} = U_L^{core}(r) + \sum_\ell \sum_m |\ell m> \left[U_\ell^{core}(r) - U_L^{core}(r) \right] <\ell m| \qquad (79)$$

where L is taken at least as large as the highest angular momentum orbital occupied in the core. The term $U_L^{core}(r)$ represents the effective Coulomb and exchange potential felt by the valence electrons. The second term essentially accounts for the repulsive potential between valence and core electrons for each symmetry ℓ. The only non-local character exhibited by a potential of the form of Equation (79) arises from the ℓ-dependence which can be cast in terms of one-electron integrals between the core and valence orbitals. Explicit two-electron terms connecting core and valence orbitals are thus avoided which greatly simplifies the calculation of matrix elements of the effective Hamiltonian. The potential given by Equation (79) can be compared with the generalized Phillips-Kleinman pseudo-potential (Reference 59).

$$(80)$$

$$U^{core} = \sum_c (2J_c - K_c) + V^{CO}$$

where J_c and K_c represent the core orbital Coulomb and exchange operators and V^{CO} is a complicated non-local operator which guarantees core-valence

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orthogonality. Since the P-K core orbitals must simultaneously be eigenfunctions of both the core and valence Hartree-Fock Hamiltonians, V^{CO}, in general, contains complicated two-electron terms and limits the usefulness of Equation (80) over a full ab initio treatment.

The prescription of Kahn can be implemented by analytically fitting a nodeless pseudo-orbital, $\chi_{n\ell}$, to a linear combination of numerical or analytic Hartree-Fock orbitals determined from a full self-consistent treatment of the core electrons, using, for example, the multiconfiguration Hartree-Fock code of Froese-Fischer (Reference 67). The components, $U_\ell^{core}(r)$, of Equation (79) are then defined implicitly from the Schrödinger equation

$$\left[-\frac{\nabla^2}{2} - \frac{z}{r} + U_\ell^{core}(r) + 2J_{val} - K_{val}\right] \chi_{n\ell} = \epsilon_{n\ell} \, \chi_{n\ell} \tag{81}$$

whereby

$$U_\ell^{core}(r) = \epsilon_{n\ell} + \frac{z}{r} + \frac{1}{\chi_{n\ell}} \left[\frac{\nabla^2}{2} - 2J_{val} + K_{val}\right] \chi_{n\ell} \tag{82}$$

Equation (81) can be extended to relativistic systems in several ways. Kahn, et al (Reference 68) suggest an approximate treatment of adding only the mass-velocity and Darwin terms to the usual electrostatic Hamiltonian and to determine approximate HF orbitals in the manner prescribed by Cowan and Griffin (Reference 52). Equation (81) is then used to determine an effective $U_\ell^{core}(r)$ such that $\epsilon_{n\ell}$ are the eigenvalues of the CG approximate relativistic solution and $\chi_{n\ell}$ are curve-fitted to the CG-HF orbitals. In this treatment, the $\chi_{n\ell}$ represent approximate solutions to the major component wavefunction, $P_{n\ell}$, determined at the center-of-gravity of the spin-orbit states.

Lee, et all (Reference 65) adopt a somewhat more complicated treatment in which the spin-orbit operator is added to the usual electrostatic Hamiltonian,

in addition to the mass-velocity and Darwin terms retained in the Cowan-Griffin treatment. The large component eigenfunctions of a full Dirac-Hartree-Fock treatment of the atom, as given, for example, by Desclaux (Reference 69) are then curve-fitted in a manner similar to the Kahn treatment but include the additional index for the particular spin-orbit state, $\chi_{n\ell j}$. Use of these eigenfunctions in a molecular system fits more naturally into a (J-J) coupling scheme whereas the $\chi_{n\ell}$ determined using the Kahn method are more easily represented using Λ-s coupling.

Although these effective core models can often accurately describe an atomic eigenvalue sequence, including even high-lying electronically excited states (Reference 70), there are inherent difficulties in their application to molecular environments, where the maximum angular momentum component of the valence shell orbitals may often exceed the highest ℓ-value component retained in Equation (82). This is particularly true for valence orbitals which exhibit strong changes from atomic form through hybridization with higher angular momentum orbitals or through the addition of more compact polarizaiton terms. In either case, since the relativistic terms are now all buried in a fixed rather than a dynamic relativistic operator, only static core effects are imposed in determining the shape of the valence molecular orbitals. Relativistic effects between valence electrons and shielding effects of the core by the valence electrons are therefore neglected in these effective core treatments. In addition, the models obviously break down completely when the nuclei are brought together to dimensions such that core overlap and polarization effects become significant. Unfortunately, calculations to date seem to indicate that such effects begin to set in for internuclear separations of the order of equilibrium bond lengths.

SECTION 4

DISCUSSION OF RESULTS

A preliminary study of the electronic structure of U, U^+, UO and UO^+ had previously been undertaken by UTRC. Both Hartree-Fock-Slater (Reference 71) and screened hydrogenic (Reference 72) wavefunctions had been used to find optimum 7s, 5f, and 6d orbitals. Only small differences in the orbitals were found between these two approaches and the calculated orbitals were fitted to LCAO expansions using an effective nuclear charge Hamiltonian. The energies of the various possible sublevels of the ground state configuration for U $(7s^2 5f^3 6d;$ 158 terms) and U^+ $(7s^2 5f^3;$ 17 terms) were then calculated using these effective nuclear charges. These calculated term levels are in good agreement with the experimental studies of Kiess, et al. (Reference 73) for U and the group-theoretical treatment of Elliott, et al. (Reference 74) for U^+. Relativistic corrections and spin-orbit splitting factors were estimated using perturbation theory based on a one-electron model. It was found that L-S coupling is a reasonable approximation for many multiplets of these systems, provided there is little configuration mixing or promotion from the 7s orbitals, which are found to have strong relativistic corrections. Departure from pure L-S coupling among the 5f electrons was estimated to be less than 10 percent (Reference 75). A complete (J-J) coupled analysis of U and U^+ was not carried out in these preliminary studies.

An analysis of the electronic structure of UO and UO^+ using a relativistic formulation was undertaken by UTRC under this Contract. The possible low-lying molecular states are shown in Tables 1 and 5. Preliminary calculations were performed for several states of UO and UO^+ and for the ground state of UO_2, UO_2^+ and UO_2^{++}. A brief summary of the results of these molecular calculations follows.

UO

Electronic structure calculations were carried out for this system using a relativistic density functional formalism. Only a selected group of symmetries was studied. Our calculations indicate that the lowest symmetry of UO is derived from the (Λ,S) coupled ^5I state and has the following principal molecular orbital occupancy:

$$^5I \; [1\sigma^2 \; 2\sigma^2 \; 3\sigma^2 \; 4\sigma^2 \; 1\pi^4 \; 2\pi^4 \; \vdots \; 3\pi \; 1\delta \; 1\phi \; \vdots \; 5\sigma] \qquad (83)$$
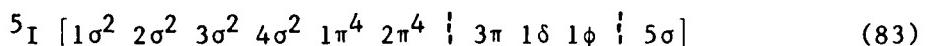
The $\vdots \; 3\pi \; 1\delta \; 1\phi \; \vdots$ group derives from the $5f^3$ atomic configuration in the U atom and is quartet coupled. We have found that the ^5I state of UO is the ground state but that several other symmetries, including ^5K and ^3I, are low-lying. The results are shown in Figure 1 which indicates that only states of triplet or quintet multiplicity are bound for this system. An examination of the structure of these low-lying states of UO indicates a near total charge transfer to $U^{+2}O^{-2}$ for short (equilibrium) internuclear separations. Thus only the molecular states in the lower group shown in Table 1 are likely to be bound. This would yield 42 bound molecular states arising from $U[^5L] + O[^3P]$ and 39 repulsive states. Since (J-J) coupling is surely a better approximation for UO, these two manifolds of states will be optically connected and many pre-dissociation paths of the type:

$$UO^{*\ddagger} + h\nu \rightarrow UO^{**} \rightarrow U + O \qquad (84)$$
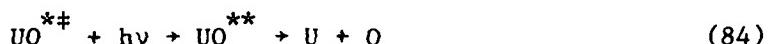
are possible. Here $UO^{*\ddagger}$ is a vibrationally excited low-multiplet state of UO and UO^{**} is a dissociating state. The predicted optical absorption should be strong since the transfer is from highly ionic states to neutral valence states of UO. Since UO has a large dissociation energy (7.87 eV), both one photon and two photon solar excitation processes are possible.

A vibrational analysis of the $\Omega = 5$ ground state of UO was carried out using a Hulbert-Hirshfelder (Reference 76) fit to our calculated potential curves. This fit yields an equilibrium internuclear distance of 1.90 Å and a fundamental vibrational constant (ω_e) of 859 cm^{-1}. The spin-orbit interaction was calculated using U^{+2} atomic splitting parameters. No explicit two-center effects are included. Our calculated spectroscopic data are compared in Table 2 with the work of Krauss and Stevens (Reference 77) and estimates based on experimental data for similar systems. The agreement is well within the uncertainty of the calculations or experimental estimates.

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An analysis of the LWIR emission from UO was carried out based on the ground ^5I electronic state. These calculations should also be representative of the LWIR emission from other low-lying electronic states since they exhibit similar ionicities. Our calculated f-numbers, including fundamentals and overtones, are given in Table 3. These data (v' > v") are given for the lowest 30 vibrational levels. We have also included the emission wavelengths for each transition. For UO, our calculated f-number for the 1-0 transition is 4.86×10^{-5} at $\lambda = 12.04$ μ. In Table 4, we present the calculated integrated band absorption coefficients as a function of temperature. All overtone contributions have been included in these band absorption coefficients.

UO^+

Detailed searches of several symmetries of UO^+ were carried out to determine the ground molecular state of this system. Our calculations indicate that the lowest symmetry of UO^+ is derived from the (Λ, S) coupled ^4I state and has the following principal molecular orbital occupancy:

$$^4I \left[1\sigma^2 \ 2\sigma^2 \ 3\sigma^2 \ 4\sigma^2 \ 1\pi^4 \ 2\pi^4 \ \vdots \ 3\pi \ 1\phi \ 1\delta \ \vdots \right] \qquad (85)$$
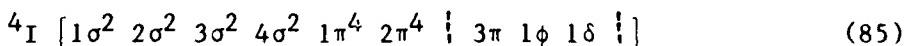
Again we find that the $\vdots$ 3π 1ϕ 1δ $\vdots$ group is quartet coupled in the ground state but a second manifold of states for the UO^+ system, which exhibit doublet coupling of these electrons, lies about 2 eV above the ground state. An apparent gap in the density of states for UO^+ is found between these two groups.

Calculations for UO^+ proved to be much more complex than UO owing to the presence of at least two low-lying dissociation limits of $U^+ + 0$. As indicated in Table 5, the ionic $U^{++}0^-$ structures will mix in all multiplicities with molecular ion states arising from $U^+[^4I] + 0[^3P]$, $U^+[^6L] + 0[^3P]$, and $U^+[^6K] + 0[^3P]$. Thus, this system may not exhibit the repulsive valence states that were found for UO.

A vibrational analysis of the $\Omega = 9/2$ ground state of UO^+ was carried out using a Hulbert-Hirschfelder (Reference 76) fit to our calculated potential

..... The spin-orbit splittings were derived from atomic parameters for the
... ... ds an equilibrium internuclear distance of 1.84 Å and a
fundamental vibrational constant of 890 cm^{-1}. These data are compared in
Table ... with other calculated estimates, since there are no experimental data
available. The agreement between our work and that of Krauss and Stevens
(Reference ...) is less satisfactory than in the case of UO but still well
within the uncertainty of the several calculations.

A perturbative treatment for calculating the density of states in uranium
molecules is available through the use of ligand field theory. The basic
concept relies on the assumption that the structure and density of the 5f
electrons in uranium and its ions remain unchanged in a molecular environment.
Our calculated multiplet splitting for the 5f electrons in U^+ is given in
Table 6. This clearly indicates that the ^4I component of $5f^3$ is low-lying and
that the lowest doublet manifold lies ~ 2.2 eV above the ground state. If
this splitting carries over to the UO^+ ion without much change, the following
solar pumped process is possible:

$$UO^+[^4I] + h\nu \rightarrow UO^{+*}[^2H]$$

$$e + UO^{+*}[^2H] \rightarrow U[^5L] + O[^3P]$$

(86)
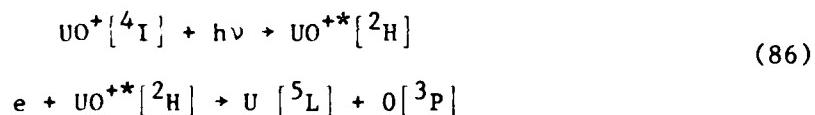
Dissociative-recombination is not energetically possible from the ground ^4I
state of UO^+ but it is possible from the excited ^2H and higher states. The
optical connections between these two manifolds of UO^+ states will be studied
in future work.

An analysis of the emission characteristics for the ground state of UO^+
indicates an oscillator strength for emission (f_{10}) of 5.17 x 10^{-5} at λ =
11.3 μ. A complete analysis of our calculated LWIR emission for UO^+ is given
in Table 7 for the lowest 30 vibrational levels. In Table 8, we present our
calculated integrated band absorption coefficients for UO^+. A detailed
analysis of the vibrational - rotational spectra and band absorption/emission
characteristics for these systems, UO and UO^+, is currently in progress.

Our calculated LWIR emission for UO^+ is typical of that for a highly
ionic metal oxide. We predict strong emission from the fundamentals of UO^+ in

the wavelength region 11.3 ~ 14 μ. Since this system exhibits weak
anharmonicity, we fine the overtones down in intensity by several orders of
magnitude. However, the first excited state of UO^+ (^4H) lies at ~ 2800 cm^{-1}
in our calculations with a predicted electronic oscillator strength of ~ 1 x
10^{-5} for the $^4I - ^4H$ transition. An analysis of the spin-orbit splitting of
the excited ^4H manifold has not yet been carried out but the predicted result
is that the lowest $^4H_{7/2}$ component should lie at ~ 1500 cm^{-1} with a similar
oscillator strength (~ 1 x 10^{-5}) for the $^5I_{9/2} - ^5H_{7/2}$ transition. Thus the
electronic and vibrational manifolds for UO^+ are highly overlapped above the
second vibrational level of the ground $^5I_{9/2}$ state. Since the density of
electronic states of UO^+ is very large above ~ 2.2 eV, we predict that strong
solar pumping, followed by intense radiation in the region 0.6 $\widetilde{<} \lambda \widetilde{<}$ 11.3 μ
should occur for this system. This conclusion is similar to that reached by
Krauss and Stevens (Reference 77) based on their MCSCF analysis of the UO^+
system. Since the excited electronic states of UO^+ lying in the region of
strong solar flux (.4 - .7 μ) exhibit shifted equilibrium internuclear
separation from that of the ground ^4I state, we predict efficient conversion
of solar photons to IR photons for this system.

UO_2

Our calculations of the triatomic species, UO_2, have indicated two low-
lying electronic states in $D_{\infty h}$ symmetry. Their principle molecular orbital
occupancies are:

$$^3H_u \left[1\sigma g^2\ 1\sigma u^2\ 2\sigma g^2\ 1\pi u^4\ 2\sigma u^2\ 3\sigma g^2\ 2\pi u^4\ 1\pi g^4\ 3\sigma u^2 \mid 1\delta g\ 1\phi u \right]$$

$$^5I_u \left[1\sigma g^2\ 1\sigma u^2\ 2\sigma g^2\ 1\pi u^4\ 2\sigma u^2\ 3\sigma g^2\ 2\pi u^4\ 1\pi g^4\ 3\sigma u \mid 3\pi u\ 1\delta g\ 1\phi u \right]$$

(87)

The lowest ^3H_u state corresponds to an ionicity of $O^=U^{+4}O^=$, whereas the ^5I_u
state indicates back-bonding from the oxygen ligands into the stable $5f^3$ sub-
structure of uranium. A third low-lying ^5I_g structure is also found which
corresponds to a $3\sigma_u \rightarrow 4\sigma_g$ promotion out of the second configuration given
above. More detailed calculations of this system are indicated but our

preliminary data indicate that UO_2 should exhibit an integrated band absorption/emission coefficient in the LWIR of between 1.5 - 2.0 times that calculated for UO.

UO_2^+

A preliminary analysis of UO_2^+ has been carried out in $D_{\infty h}$ symmetry. McGlynn and Smith (Reference 78) have proposed a $^2\Phi_u$ ground state for this ion based on simple molecular orbital arguments. Their set of one-electron orbital energies is based on a maximum overlap criterion that is empirical in character. More modern calculations of the actinide series atoms suggest that a $U^{+5}[O^{-2}]_2$ or $U^{+3}[O^{-1}]_2$ structure should be the most stable configuration. In terms of MO's, the lowest predicted electronic states ($D_{\infty h}$) would be:

$$1\sigma g^2 \ 1\sigma u^2 \ 2\sigma g^2 \ 1\pi u^4 \ 2\sigma u^2 \ 3\sigma g^2 \ 2\pi u^4 \ 1\pi g^4 \ 3\sigma u^2 \ \Big| \ 1\phi u \ : \ ^2\Phi_u$$

or
$$\hspace{9cm} (88)$$

$$1\sigma g^2 \ 1\sigma u^2 \ 2\sigma g^2 \ 1\pi u^4 \ 2\sigma u^2 \ 3\sigma g^2 \ 2\pi u^4 \ 1\pi g^4 \ 3\sigma u \ \Big| \ 1\delta g \ 1\phi u \ : \ ^4H_g$$
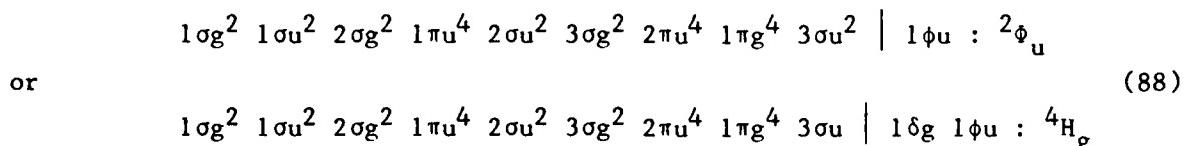
Further calculations should be carried out to determine which of these configurations has lower energy and to examine several other possible low-lying excited states. Our calculations to date indicate that the $^2\Phi_u$ symmetry is the ground state. If the highly ionic $^2\Phi_u$ state, as predicted by McGlynn, is in fact the ground state, the radiation/absorption characteristics of UO_2^+ should be approximately twice as strong as UO^+. No real quantitative information about the absorption spectrum of UO_2^+ is available at present but McGlynn predicts a strong $^2\Phi_{7/2u} \rightarrow {}^2\Delta_{5/2g}$ transition at $\lambda \overset{\sim}{-} 0.4\mu$. Again, this transition lies in the peak solar flux region.

There appear to be many strong optical absorption bands in this system corresponding to molecular orbital transitions between MO's derived from f→d uranium atom symmetries. There are also some large ligand to central uranium atom charge transfer effects corresponding to transitions between the two types of configurations listed above. Our preliminary data indicate that UO_2^+ should possess a rich LWIR spectra and should exhibit many strong electronic bands ($f \sim 10^{-2} - 10^{-1}$) beginning at ~ 500 nm.

UO_2^{++}

An extensive set of calculations for the ground state of UO_2^{++} was carried out in $D_{\infty h}$ symmetry. The ground electronic state has the dominant molecular orbital configuration:

$$^1\Sigma_g^+: \left[1\sigma g^2\ 1\sigma u^2\ 2\sigma g^2\ 1\pi u^4\ 2\sigma u^2\ 3\sigma g^2\ 2\pi u^4\ 1\pi g^4\ 3\sigma u^2\right] \qquad (89)$$
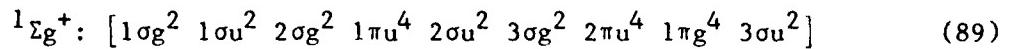
We find an equilibrium internuclear separation of 2.06 Å, a value somewhat larger than that corresponding to the ion in solution ($\sim$ 1.7 Å). At present it is uncertain whether this represents a deficiency in the calculations or whether significant back-bonding of electron charge to the central uranium atom is occurring in the gas phase UO_2^{++} species. This would result in a lengthing of the U-O bond and a corresponding decrease in the U-O bond strength.

The first excited electronic state of UO_2^{++} corresponds to a $3\sigma u \rightarrow 1\phi g$ electron promotion. This lies at $\sim$ 3.6 eV and we therefore predict very weak solar pumping for this species. The LWIR analysis should be carried out, however, since the highly ionic nature of UO_2^{++} may give rise to a strong absorption/emission character for the asymmetric stretch vibrational mode.

SECTION 5

RECOMMENDATIONS

The low-lying molecular states of UO^+ arising from ^4I $(5f^37s^2)$, $^6L(5f^37s6d)$, and $^6K(5f^37s6d)$ of U^+ are given in Table 2. Additional low-lying states of UO^+ arise from the $^6M(5f^36d7p)$ state of U^+ and from the doubly ionized $^5L(5f^36d)$ and $^5I(5f^37s)$ and triply ionized $^4I(5f^3)$ states of the uranium ion. Further calculations of the term manifold for this molecular ion are needed. In our preliminary studies, a separate (higher lying) chemistry was found for U^+ when the 5f electrons were doublet spin-coupled. Verification of this structure, using a relativistic framework for this ion, is an area of proposed research.

Finally, theoretical studies of UO^{++}, UO_2^+ and the uranyl (UO_2^{++}) ion should be undertaken. The UO_2^+ ion has the indicated ground state configuration:

$$^2\Phi_u \left[1\sigma g^2 \; 1\sigma u^2 \; 2\sigma g^2 \; 1\pi u^4 \; 2\sigma u^2 \; 3\sigma g^2 \; 2\pi u^4 \; 1\pi g^4 \; 3\sigma u^2 \; 1\phi u \right] \qquad (90)$$
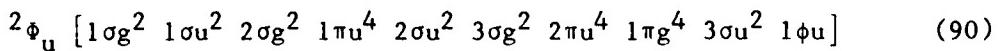
where the composition of the various molecular orbitals is given below:

Molecular Orbital	Composition
$1\sigma g$	6s(U)
$1\sigma u$, $2\sigma g$	2s(O)
$1\pi u$, $2\sigma u$	6p(U)
$3\sigma g$, $2\pi u$, $3\sigma u$, $1\pi g$	Mainly 2p(O) + 5f(U) + 6d(U)
$1\phi u$	5f(U)

The ordering and energetics of the low-lying symmetries of UO_2^+ is uncertain. A detailed study of this ion, examining both relativistic and spin-coupling effects is indicated as an area of proposed research. Studies in both linear and bent conformations should be carried out. These studies should include an analysis of the IR radiation properties of the ground electronic state and any possible low-lying electronic transitions in the IR region.

For most of these proposed calculations a density functional relativistic framework could be employed. Spin-orbit splittings and the degree of mixing from (Λ-S) to (J-J) coupling could be calculated using perturbation techniques. Our final relativistic wavefunctions could then be used to calculate

both the vibration-rotation and electronic transitions in these ions, that fall in the LWIR region of interest. The low-lying electronic states up to about 3 eV excitation should be included in this study.

The focus of these studies should continue to be on the U^+, UO^+ and UO_2^+ systems but a limited study of UO^{++} and UO_2^{++} is indicated. An examination of the thermodynamics of the uranium/oxygen system as given in Figure 2, shows that U^+ and UO^+ are terminal ions and therefore potentially important radiators at high altitudes, whereas UO_2^+ is more important at altitudes of significant O_2 concentration. The importance of UO^{++} and UO_2^{++} is not well known owing to the uncertainty in the thermodynamics of these ions. It is anticipated that continued theoretical studies will clear up many of the current uncertainties in the radiation characteristics of these systems.

Follow-on studies should also include an analysis of the several possible kinetic pathways that have been suggested by our work to date. These include photoexcitation and photodissociation of UO as:

$$U^+O^- + h\nu \rightarrow UO*$$
$$UO* + h\nu \rightarrow U + O \tag{91}$$

where UO* represents the excited neutral valence states of UO. Other potentially important kinetic studies include dissociative-recombination routes from

$$e + \left[UO^+\right]^* \rightarrow U* + O \tag{92}$$

where $\left[UO^+\right]^*$ is an electronically excited state of UO^+ which exhibits doublet coupling for the 5f electrons and charge transfer processes such as

$$U^{++} + O \rightarrow U^+ + O^+ \tag{93}$$

In addition, the dissociative-recombination routes

$$
\begin{aligned}
e + UO^{++} &\rightarrow & U^+ + O \\
e + UO_2^{++} &\rightarrow & U + O_2^+ \\
&\rightarrow & U^+ + O + O \quad\quad (94) \\
&\rightarrow & UO + O^+ \\
&\rightarrow & UO^+ + O
\end{aligned}
$$
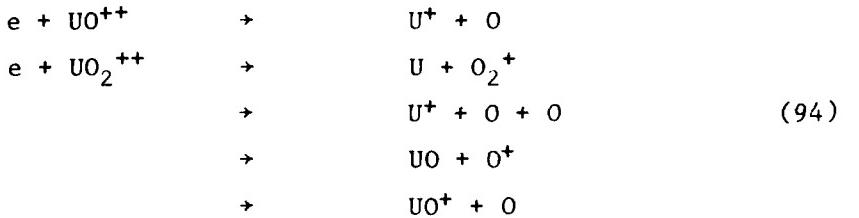
are uncertain until the energetics of the doubly ionized UO^{++} and UO_2^{++} species are better defined.
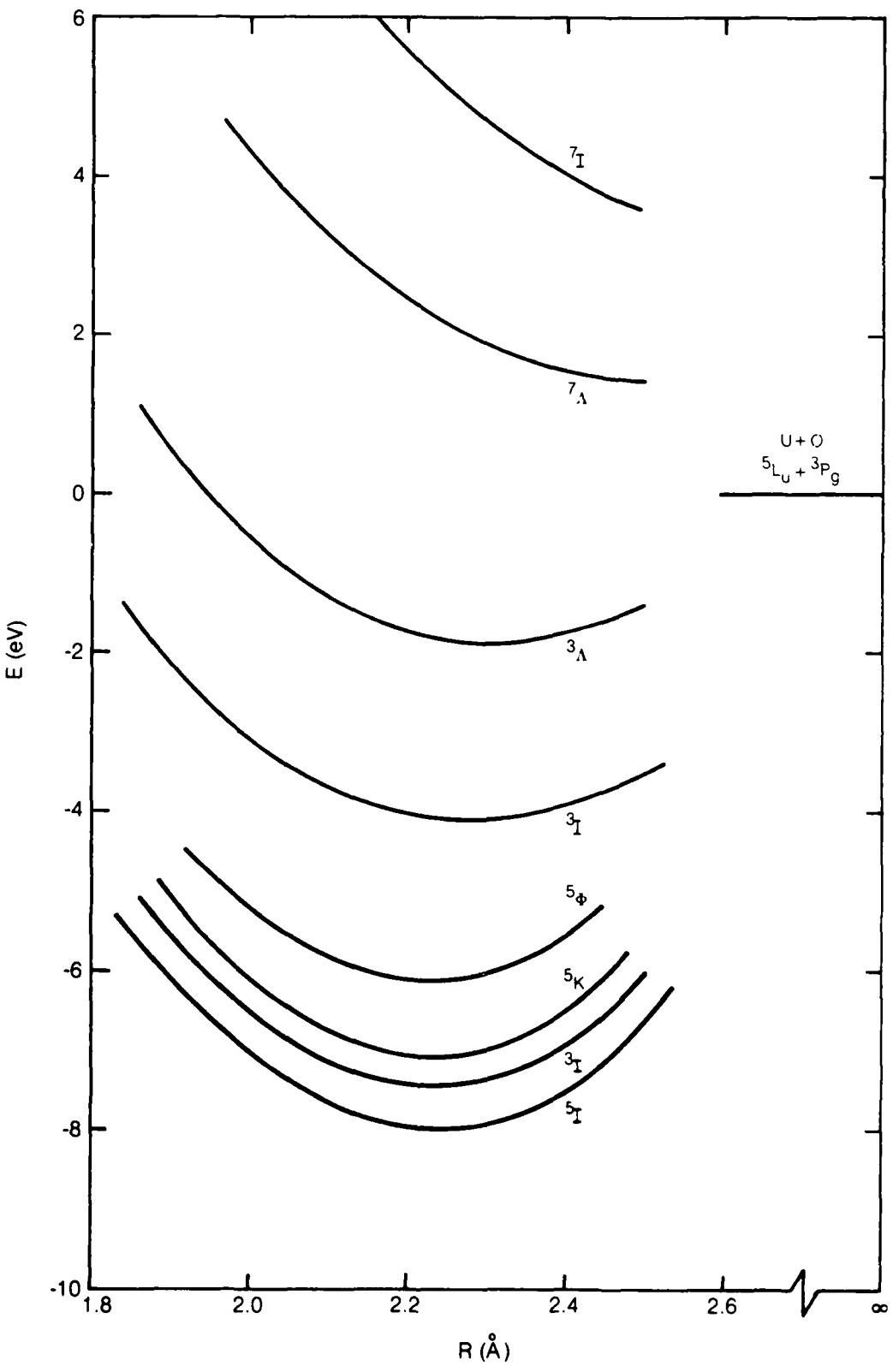
Figure 1. Relativistic (Λ, S) UO potential energy curves.

82-5-82-1

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ENERGY (eV)

U + O + O^{++} (63 84)

60.0   UO + O^{++} (56 28)

55.0

50.0   U + O$_2$$^{++}$ {46 2}

45.0   U + O$^+$ + O$^+$ (42 3)

40.0

35.0   U$^+$ + O$^+$ + O   (34.80)
                       U^{++} + O + O   (32.65)

30.0   U$^+$ + O$_2$$^+$ (28.10)   U + O + O$^+$ (28.69)
         U^{++} + O$_2$ (27.54)
         UO$^+$ + O$^+$ (26.85)
                       UO^{++} + O   [25.0]
25.0
                       UO$_2$$^{++}$ U + O$_2$$^+$ (21.99)
                                        U$^+$ + O + O   (21.19)
                                        UO + O$^+$ (21.13)
20.0   U$^+$ + O$_2$ (16.08)

         19.0 LASL
         22.0 UTRC (EST.)
         22.2 UTRC (CALC.)   U + O + O   (15.08)
15.0   UO$^+$ + O   (13.24)

                                                            U + O$_2$ (9 97)
10.0
                                                            UO + O   (7 52)
                       UO$_2$$^+$ (5.50)
5.0

                                                            UO$_2$ (0 00)
0.0

[ ] UNCERTAIN   80–7–116–1
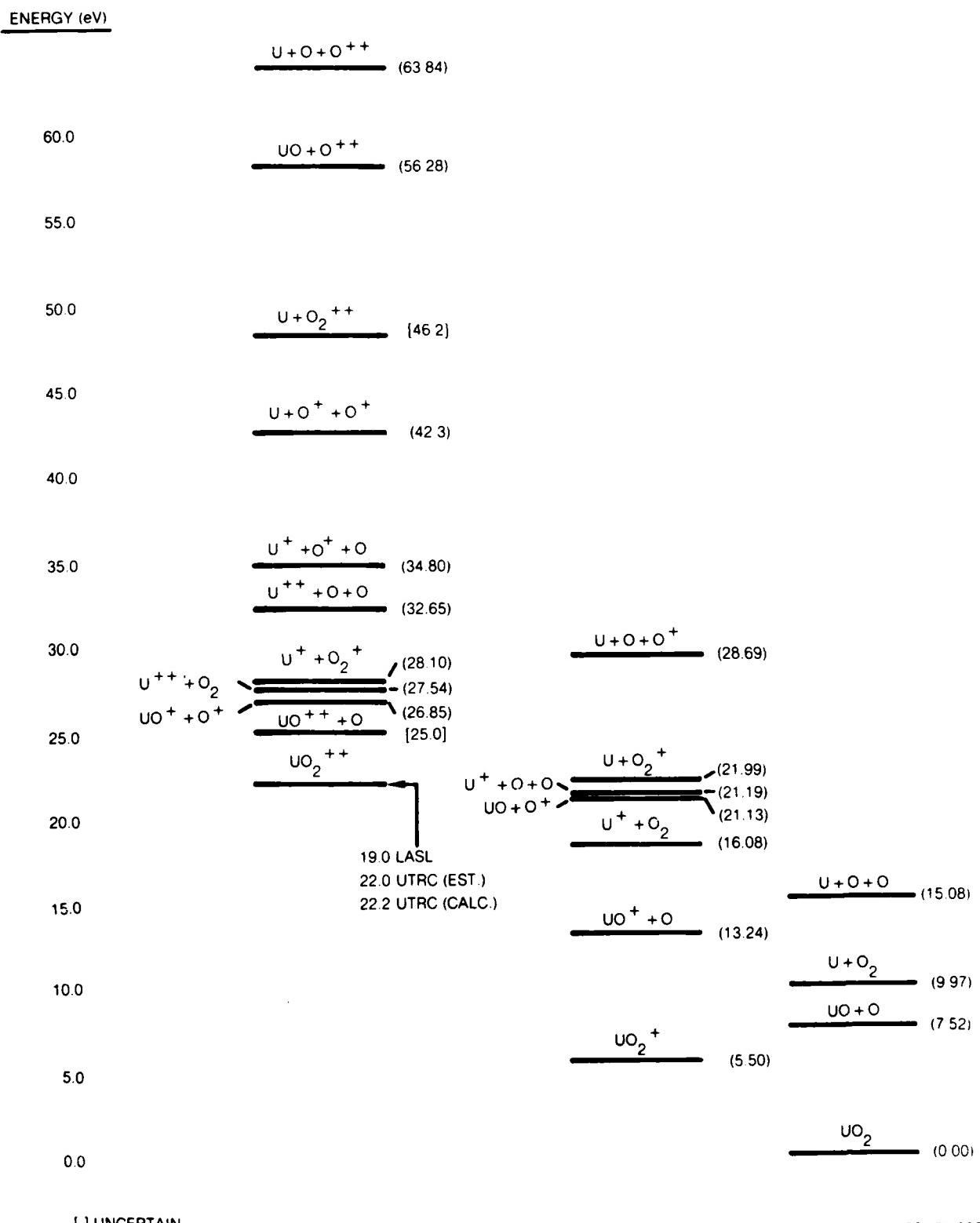
Figure 2. Thermodynamic stability of known uranium/oxygen species.

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Table 1. Molecular states of UO.

<table>
<tr><td><u>Separated Atom</u></td><td><u>Molecular States</u></td></tr>
</table>

<u>U + O</u>

$^5L_u(5f^37s^26d) + ^3P_g(2p^4)$

$E_\infty = 0.000$ eV
(81 states)

$^3\Sigma^-(1)$, $^3\Sigma^+(2)$, $^5\Sigma^-(1)$, $^5\Sigma^+(2)$, $^7\Sigma^-(1)$,

$^7\Sigma^+(2)$, $^3\Pi(3)$, $^5\Pi(3)$, $^7\Pi(3)$, $^3\Delta(3)$, $^5\Delta(3)$,

$^7\Delta(3)$, $^3\Phi(3)$, $^5\Phi(3)$, $^7\Phi(3)$, $^3\Gamma(3)$, $^5\Gamma(3)$,

$^7\Gamma(3)$, $^3H(3)$, $^5H(3)$, $^7H(3)$, $^3I(3)$, $^5I(3)$,

$^7I(3)$, $^3K(3)$, $^5K(3)$, $^7K(3)$, $^3\Lambda(2)$, $^5\Lambda(2)$,

$^7\Lambda(2)$, $^3M(1)$, $^5M(1)$, $^7M(1)$

$^5K_u(5f^37s^26d) + ^3P_g(2p^4)$

$E_\infty = 0.096$ eV
(72 states)

$^3\Sigma^-(2)$, $^3\Sigma^+(1)$, $^5\Sigma^-(2)$, $^5\Sigma^+(1)$, $^7\Sigma^-(2)$, $^7\Sigma^+(1)$,

$^3\Pi(3)$, $^5\Pi(3)$, $^7\Pi(3)$, $^3\Delta(3)$, $^5\Delta(3)$, $^7\Delta(3)$,

$^3\Phi(3)$, $^5\Phi(3)$, $^7\Phi(3)$, $^3\Gamma(3)$, $^5\Gamma(3)$, $^7\Gamma(3)$,

$^3H(3)$, $^5H(3)$, $^7H(3)$, $^3I(3)$, $^5I(3)$, $^7I(3)$,

$^3K(2)$, $^5K(2)$, $^7K(2)$, $^3\Lambda(1)$, $^5\Lambda(1)$, $^7\Lambda(1)$

Table 1. Molecular states of UO. (Continued)

Separated Atom

Molecular States

$U^+ + O^-$

$^4I_u(5f^37s^2) + {}^2P_u(2p^5)$

(42 states)

$^3\Sigma^+(1)$, $^5\Sigma^+(1)$, $^3\Sigma^-(2)$, $^5\Sigma^-(2)$, $^3\Pi(3)$,

$^5\Pi(3)$, $^3\Delta(3)$, $^5\Delta(3)$, $^3\Phi(3)$, $^5\Phi(3)$,

$^3\Gamma(3)$, $^5\Gamma(3)$, $^3H(3)$, $^5H(3)$, $^3I(2)$,

$^5I(2)$, $^3K(1)$, $^5K(1)$

$U^{++} + O^=$

$^5L_u(5f^36d) + {}^1S_g(2p^6)$

(9 states)

$^5\Sigma^-(1)$, $^5\Pi(1)$, $^5\Delta(1)$, $^5\Phi(1)$, $^5\Gamma(1)$,

$^5H(1)$, $^5I(1)$, $^5K(1)$, $^5\Lambda(1)$

Table 2.   Calculated spectroscopic data for UO/UO$^+$

	UO [^5I]		UO$^+$ [^4I]	
ω_e (cm^{-1}):	820	(matrix)	949	(SCF)
	836	(scaled from ThO)	935	(MCSCF)
	863	(SCF)*	925	(MCSCF: $\Omega = 9/2$)
	845	(MCSCF)	890	(RDF-UTRC)
	859	(RDF-UTRC)		
$\omega_e x_e$(cm^{-1}):	2.7	(H-H potential)	2.7	(H-H potential)
	12.0	(^3I excited state)		
R_e(Å):	1.84	(matrix)	1.83	(SCF)
	1.88	(SCF)	1.84	(MCSCF)
	1.84	(MCSCF-Krauss)	1.84	(RDF-UTRC)
	1.90	(RDF-UTRC)		

*SCF and MCSCF results, see Reference 77.

Table 3-1. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of UO(X5I-X5I).

V'\V"	0	1	2	3	4	5	6	7	8	9
0	– –	– –	– –	– –	– –	– –	– –	– –	– –	– –
1	* 4.86-05 ** 12.04	– –	– –	– –	– –	– –	– –	– –	– –	– –
2	1.57-07 6.04	9.69-05 12.12	– –	– –	– –	– –	– –	– –	– –	– –
3	9.82-10 4.04	4.69-07 6.08	1.45-04 12.20	– –	– –	– –	– –	– –	– –	– –
4	8.10-12 3.04	3.89-09 4.07	9.35-07 6.12	1.93-04 12.28	– –	– –	– –	– –	– –	– –
5	4.51-14 2.44	4.01-11 3.06	1.00-08 4.09	1.56-06 6.16	2.40-04 12.36	– –	– –	– –	– –	– –
6	7.41-17 2.04	9.87-13 2.46	1.35-10 3.08	2.02-08 4.12	2.33-06 6.20	2.87-04 12.44	– –	– –	– –	– –
7	7.62-15 1.75	1.03-13 2.05	2.63-12 2.47	3.29-10 3.10	3.51-08 4.15	3.26-06 6.24	3.34-04 12.53	– –	– –	– –
8	1.25-14 1.54	2.27-15 1.77	1.97-13 2.07	5.55-12 2.49	6.45-10 3.12	5.61-08 4.18	4.34-06 6.28	3.80-04 12.61	– –	– –
9	8.66-17 1.37	2.36-16 1.55	7.91-16 1.78	1.19-13 2.08	1.22-11 2.51	1.15-09 3.14	8.42-08 4.20	5.57-06 6.33	4.26-04 12.69	– –

* oscillator strength
** wavelength, microns

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Table 3-2. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO(X^5I - X^5I)$.

v'\v"	0	1	2	3	4	5	6	7	8	9
10	*5.39-15 **1.24	7.60-16 1.38	2.34-14 1.56	1.14-15 1.79	1.80-13 2.09	2.48-11 2.52	1.94-09 3.16	1.20-07 4.23	6.95-06 6.37	4.72-04 12.78
11	2.96-15 1.13	4.26-15 1.25	7.60-15 1.39	1.42-14 1.57	2.21-15 1.80	4.89-13 2.11	4.63-11 2.54	3.06-09 3.18	1.65-07 4.26	8.49-06 6.41
12	5.17-17 1.04	2.92-15 1.14	9.74-19 1.26	9.37-15 1.40	1.44-15 1.58	7.30-15 1.81	1.06-12 2.12	7.77-11 2.56	4.60-09 3.21	2.20-07 4.29
13	1.23-15 0.96	2.78-16 1.05	1.36-16 1.15	4.27-16 1.27	3.94-15 1.41	4.24-17 1.59	5.68-15 1.83	1.74-12 2.14	1.25-10 2.57	6.61-09 3.23
14	4.59-16 0.90	3.80-15 0.97	3.52-16 1.05	3.84-15 1.15	1.49-17 1.27	3.81-15 1.42	3.56-15 1.60	7.57-15 1.84	2.53-12 2.15	1.96-10 2.59
15	9.18-19 0.84	1.42-15 0.90	1.67-15 0.98	8.07-16 1.06	2.67-15 1.16	2.09-15 1.28	5.06-15 1.43	1.85-14 1.61	1.53-14 1.85	3.88-12 2.17
16	1.23-16 0.79	1.37-16 0.85	1.05-15 0.91	1.25-17 0.98	4.45-16 1.07	3.39-16 1.17	5.32-15 1.29	9.59-15 1.44	2.47-14 1.63	2.97-15 1.86
17	9.47-17 0.75	1.08-15 0.80	1.42-16 0.85	7.14-19 0.92	3.31-16 0.99	6.11-16 1.08	2.56-16 1.18	3.49-15 1.30	3.13-14 1.45	2.32-14 1.64
18	1.75-17 0.71	4.13-16 0.75	1.92-15 0.80	1.81-16 0.86	3.64-16 0.92	2.01-16 0.99	1.11-15 1.08	1.93-15 1.19	4.97-15 1.31	3.56-14 1.46
19	1.58-18 0.67	3.18-21 0.71	1.05-15 0.76	8.64-16 0.81	7.15-17 0.86	5.47-16 0.93	3.55-17 1.00	6.64-17 1.09	2.55-16 1.19	1.04-14 1.32

* oscillator strength
** wavelength, microns

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Table 3-3. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of UO(X^5I-X^5I).

v'\v''		0	1	2	3	4	5	6	7	8	9
20	*	2.07-17	1.00-16	8.79-18	5.50-16	9.08-17	2.79-17	8.85-16	1.15-15	9.28-18	6.23-17
	**	0.64	0.68	0.72	0.76	0.81	0.87	0.94	1.01	1.10	1.20
21		2.03-17	9.87-17	6.65-16	1.91-17	1.04-16	1.27-19	1.58-16	8.02-20	1.24-15	3.91-16
		0.61	0.65	0.68	0.72	0.77	0.82	0.88	0.94	1.02	1.11
22		2.88-18	3.95-17	5.02-16	7.53-16	3.17-18	1.55-17	2.44-16	3.27-16	7.10-16	1.18-16
		0.59	0.62	0.65	0.69	0.73	0.77	0.82	0.88	0.95	1.03
23		1.98-18	3.38-18	2.96-17	6.50-16	3.12-16	8.45-18	1.59-16	3.32-17	2.45-16	3.66-16
		0.56	0.59	0.62	0.65	0.69	0.73	0.78	0.83	0.89	0.96
24		6.74-18	8.64-18	6.20-17	2.22-17	4.78-16	2.63-16	1.17-19	3.25-16	4.27-16	4.45-18
		0.54	0.57	0.60	0.63	0.66	0.70	0.74	0.78	0.84	0.90
25		2.94-18	3.84-17	1.26-16	1.87-16	9.32-17	3.26-16	4.55-18	1.87-20	3.84-17	8.13-16
		0.52	0.55	0.57	0.60	0.63	0.66	0.70	0.74	0.79	0.84
26		4.40-20	3.17-17	6.13-17	2.71-16	8.25-17	2.62-17	7.83-17	1.35-16	1.01-16	2.02-16
		0.50	0.53	0.55	0.58	0.60	0.63	0.67	0.71	0.75	0.80
27		3.86-19	2.28-18	5.83-18	5.81-17	3.85-16	1.26-16	1.08-17	3.53-18	6.91-17	9.46-17
		0.49	0.51	0.53	0.55	0.58	0.61	0.64	0.67	0.71	0.75
28		4.17-19	9.27-18	5.99-18	2.33-18	2.32-16	3.77-16	8.82-17	4.33-17	1.40-16	1.76-17
		0.47	0.49	0.51	0.53	0.56	0.58	0.61	0.64	0.68	0.72
29		2.09-19	2.37-17	2.82-17	2.44-17	4.08-18	2.33-16	2.39-16	4.18-19	3.49-18	8.19-17
		0.45	0.47	0.49	0.51	0.54	0.56	0.59	0.62	0.65	0.68

* oscillator strength
** wavelength, microns

Table 3-4. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of UO(X^51-X^51).

$v'\backslash v''$	10	11	12	13	14	15	16	17	18	19
10	--	--	--	--	--	--	--	--	--	--
11	* 5.17-04 ** 12.87	--	--	--	--	--	--	--	--	--
12	1.02-05 6.46	5.62-04 12.96	--	--	--	--	--	--	--	--
13	2.86-07 4.32	1.20-05 6.50	6.07-04 13.05	--	--	--	--	--	--	--
14	9.21-09 3.25	3.63-07 4.35	1.40-05 6.55	6.51-04 13.15	--	--	--	--	--	--
15	2.91-10 2.61	1.26-08 3.27	4.54-07 4.38	1.61-05 6.60	6.95-04 13.24	--	--	--	--	--
16	6.52-12 2.18	4.19-10 2.63	1.68-08 3.30	5.58-07 4.41	1.84-05 6.64	7.39-04 13.33	--	--	--	--
17	1.25-15 1.88	1.05-11 2.20	5.96-10 2.65	2.19-08 3.32	6.78-07 4.44	2.08-05 6.69	7.82-04 13.43	--	--	--
18	3.41-14 1.65	1.53-14 1.89	1.51-11 2.21	8.33-10 2.67	2.81-08 3.35	8.13-07 4.48	2.33-05 6.74	8.25-04 13.53	--	--
19	2.40-14 1.47	8.05-14 1.66	4.91-14 1.90	2.12-11 2.23	1.13-09 2.69	3.55-08 3.37	9.64-07 4.51	2.60-05 6.79	8.68-04 13.63	--

* oscillator strength
** wavelength, microns

Table 3-5. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO(X5^1-X5^1)$.

$v'\backslash v''$	10	11	12	13	14	15	16	17	18	19
20	* 1.79-14 ** 1.33	3.23-14 1.48	1.35-13 1.67	6.32-14 1.92	3.04-11 2.25	1.50-09 2.71	4.44-08 3.39	1.13-06 4.54	2.89-05 6.84	9.10-04 13.73
21	8.28-16 1.21	1.91-14 1.34	7.56-14 1.49	1.64-13 1.68	3.45-14 1.93	4.37-11 2.26	1.96-09 2.73	5.49-08 3.42	1.32-06 4.58	3.19-05 6.89
22	1.01-15 1.12	6.74-15 1.22	1.99-14 1.35	1.63-13 1.50	2.22-13 1.70	3.93-14 1.95	6.18-11 2.28	2.53-09 2.75	6.73-08 3.44	1.53-06 4.61
23	4.45-17 1.03	2.10-16 1.12	1.28-14 1.23	4.14-14 1.36	2.17-13 1.51	3.17-13 1.71	7.16-14 1.96	8.69-11 2.30	3.25-09 2.77	8.14-08 3.47
24	1.43-17 0.96	4.07-16 1.04	1.54-15 1.13	1.03-14 1.24	7.41-14 1.37	2.66-13 1.53	4.18-13 1.72	2.31-13 1.98	1.13-10 2.31	4.16-09 2.79
25	1.60-19 0.90	4.21-16 0.97	8.44-16 1.05	3.10-15 1.14	1.11-14 1.25	1.02-13 1.38	2.66-13 1.54	7.92-13 1.73	6.13-13 1.99	1.45-10 2.33
26	4.15-16 0.85	2.10-16 0.91	6.42-17 0.98	2.17-16 1.06	1.75-15 1.15	8.90-15 1.26	1.76-13 1.39	3.38-13 1.55	1.14-12 1.75	4.87-13 2.01
27	7.33-16 0.80	8.64-20 0.85	3.81-16 0.92	1.26-15 0.98	4.47-16 1.06	2.16-15 1.16	2.69-14 1.27	1.94-13 1.40	8.62-13 1.56	1.33-12 1.76
28	7.69-18 0.76	1.10-16 0.81	3.81-18 0.86	5.98-17 0.92	1.77-15 0.99	4.30-16 1.07	3.37-16 1.17	1.26-13 1.28	2.57-13 1.41	1.39-12 1.57
29	4.86-16 0.72	4.76-17 0.77	1.59-16 0.81	2.72-17 0.87	2.80-18 0.93	1.72-15 1.00	6.04-15 1.08	1.12-14 1.17	1.56-13 1.29	6.11-13 1.42

* oscillator strength
** wavelength, microns

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Table 3-6. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of UO($X5I$-$X5I$).

v'\v''	20	21	22	23	24	25	26	27	28	29
20	–	–	–	–	–	–	–	–	–	–
21	* 9.52-04 ** 13.83	–	–	–	–	–	–	–	–	–
22	3.50-05 6.94	9.94-04 13.93	–	–	–	–	–	–	–	–
23	1.76-06 4.64	3.83-05 6.99	1.04-03 14.04	–	–	–	–	–	–	–
24	9.74-08 3.50	2.01-06 4.68	4.17-05 7.04	1.08-03 14.14	–	–	–	–	–	–
25	5.16-09 2.81	1.16-07 3.52	2.28-06 4.71	4.52-05 7.10	1.12-03 14.25	–	–	–	–	–
26	1.93-10 2.35	6.33-09 2.83	1.37-07 3.55	2.58-06 4.75	4.89-05 7.15	1.16-03 14.36	–	–	–	–
27	4.19-13 2.02	2.42-10 2.37	7.78-09 2.85	1.60-07 3.58	2.90-06 4.79	5.28-05 7.21	1.20-03 14.48	–	–	–
28	2.31-12 1.77	7.16-13 2.04	3.07-10 2.38	9.42-09 2.87	1.88-07 3.60	3.24-06 4.82	5.68-05 7.27	1.24-03 14.59	–	–
29	1.80-12 1.58	3.15-12 1.79	6.80-13 2.05	4.01-10 2.40	1.13-08 2.89	2.18-07 3.63	3.62-06 4.86	6.09-05 7.32	1.28-03 14.70	–

* oscillator strength
** wavelength, microns

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Table 4. Total integrated absorption coefficients for UO ground state.

Temperature, °K (Wavelength, μ)	Fundamental (12.04)	First Overtone (6.04)	Second Overtone (4.04)	Third Overtone (3.04)	Total
100.	1156.665	3.728	.023	.000	1160.423
273.15	1156.581	3.823	.024	.000	1160.428
300.	1156.538	3.869	.025	.000	1160.432
500.	1155.947	4.479	.031	.000	1160.457
1000.	1153.399	6.974	.068	.001	1160.442
1500.	1150.375	9.893	.133	.002	1160.403
2000.	1147.191	12.951	.227	.005	1160.374
2500.	1143.911	16.082	.349	.010	1160.352
3000.	1140.551	19.265	.502	.017	1160.335
4000.	1133.599	25.747	.904	.041	1160.291
5000.	1125.879	32.279	1.429	.081	1159.668

The column header for the absorption coefficient reads: Absorption Coefficient, $\text{cm}^{-2}\,\text{atm}^{-1}$

Table 5. Molecular states of UO$^+$.

Separated Atom	Molecular States

U$^+$ + O

$^4I_u(5f^37s^2) + {}^3P_g(2p^4)$

$E_\infty = 6.11$ eV
(63 states)

$^2\Sigma^-(1)$, $^2\Sigma^+(2)$, $^4\Sigma^-(1)$, $^4\Sigma^+(2)$, $^6\Sigma^-(1)$,

$^6\Sigma^+(2)$, $^2\Pi(3)$, $^4\Pi(3)$, $^6\Pi(3)$, $^2\Delta(3)$, $^4\Delta(3)$,

$^6\Delta(3)$, $^2\Phi(3)$, $^4\Phi(3)$, $^6\Phi(3)$, $^2\Gamma(3)$, $^4\Gamma(3)$,

$^6\Gamma(3)$, $^2H(3)$, $^4H(3)$, $^6H(3)$, $^2I(2)$, $^4I(2)$,

$^6I(2)$, $^2K(1)$, $^4K(1)$, $^6K(1)$

$^6L_u(5f^37s6d) + {}^3P_g(2p^4)$

$E_\infty = 6.146$ eV
(81 states)

$^4\Sigma^-(1)$, $^4\Sigma^+(2)$, $^6\Sigma^-(1)$, $^6\Sigma^+(2)$, $^8\Sigma^-(1)$, $^8\Sigma^+(2)$,

$^4\Pi(3)$, $^6\Pi(3)$, $^8\Pi(3)$, $^4\Delta(3)$, $^6\Delta(3)$, $^8\Delta(3)$,

$^4\Phi(3)$, $^6\Phi(3)$, $^8\Phi(3)$, $^4\Gamma(3)$, $^6\Gamma(3)$, $^8\Gamma(3)$

$^4H(3)$, $^6H(3)$, $^8H(3)$, $^4I(3)$, $^6I(3)$, $^8I(3)$

$^4K(3)$, $^6K(3)$, $^8K(3)$, $^4\Lambda(2)$, $^6\Lambda(2)$, $^8\Lambda(2)$,

$^4M(1)$, $^6M(1)$, $^8M(1)$

$^6K_u(5f^37s6d) + {}^3P_g(2p^4)$

$E_\infty = 6.223$ eV
(72 states)

$^4\Sigma^-(2)$, $^4\Sigma^+(1)$, $^6\Sigma^-(2)$, $^6\Sigma^+(1)$, $^8\Sigma^-(2)$, $^8\Sigma^+(1)$,

$^4\Pi(3)$, $^6\Pi(3)$, $^8\Pi(3)$, $^4\Delta(3)$, $^6\Delta(3)$, $^8\Delta(3)$

$^4\Phi(3)$, $^6\Phi(3)$, $^8\Phi(3)$, $^4\Gamma(3)$, $^6\Gamma(3)$, $^8\Gamma(3)$,

$^4H(3)$, $^6H(3)$, $^8H(3)$, $^4I(3)$, $^6I(3)$, $^8I(3)$,

$^4K(2)$, $^6K(2)$, $^8K(2)$, $^4\Lambda(1)$, $^6\Lambda(1)$, $^8\Lambda(1)$

Table 5. Molecular states of UO$^+$ (Continued)

Separated Atom	Molecular States
$\underline{U^{++} + O^-}$	
$^5L_u(5f^36d) + {}^2P_u(2p^5)$	$^4\Sigma^+(1)$, $^4\Sigma^-(2)$, $^6\Sigma^+(1)$, $^6\Sigma^-(2)$, $^4\Pi(3)$,
(54 states)	$^6\Pi(3)$, $^4\Delta(3)$, $^6\Delta(3)$, $^4\Phi(3)$, $^6\Phi(3)$,
	$^4\Gamma(3)$, $^6\Gamma(3)$, $^4H(3)$, $^6H(3)$, $^4I(3)$,
	$^6I(3)$, $^4K(3)$, $^6K(3)$, $^4\Lambda(2)$, $^6\Lambda(2)$,
	$^4M(1)$, $^6M(1)$
$\underline{U^{+++} + O^=}$	
$^4I_u(5f^3) + {}^1S_g(2p^6)$	$^4\Sigma^-(1)$, $^4\Pi(1)$, $^4\Delta(1)$, $^4\Phi(1)$, $^4\Gamma(1)$,
(8 states)	$^4H(1)$, $^4I(1)$, $^4K(1)$

Table 6. Term levels for $U^{+1}(5f^37s^2)$, cm^{-1}

Term	Energy
^2F	105000.
^2G	72094.
^2F	58453.
^2D	48690.
^2H	47372.
^2L	42638.
^4D	42298.
^2I	41736.
^2P	31694.
^2D	31661.
^2K	26281.
^4G	26029.
^2G	23294.
^2H	17976.
^4S	16214.
^4F	16009.
^4I	0.

$E_{avg} = 33135$ cm^{-1}.

Table 7-1. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO^+(A^4I-A^4I)$.

Each cell lists the oscillator strength (*) over the wavelength in microns (**).

$v'\backslash v''$	0	1	2	3	4	5	6	7	8	9
0	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —
1	5.17-05 / 11.30	— —	— —	— —	— —	— —	— —	— —	— —	— —
2	1.60-07 / 5.67	1.03-04 / 11.38	— —	— —	— —	— —	— —	— —	— —	— —
3	9.63-10 / 3.79	4.79-07 / 5.71	1.54-04 / 11.45	— —	— —	— —	— —	— —	— —	— —
4	7.65-12 / 2.85	3.81-09 / 3.82	9.55-07 / 5.74	2.05-04 / 11.52	— —	— —	— —	— —	— —	— —
5	4.09-14 / 2.29	3.76-11 / 2.87	9.85-09 / 3.84	1.59-06 / 5.78	2.55-04 / 11.59	— —	— —	— —	— —	— —
6	2.42-16 / 1.91	9.56-13 / 2.30	1.27-10 / 2.89	1.98-09 / 3.86	2.39-06 / 5.82	3.05-04 / 11.67	— —	— —	— —	— —
7	7.44-15 / 1.65	1.02-13 / 1.93	2.47-12 / 2.32	3.11-10 / 2.91	3.45-08 / 3.89	3.33-06 / 5.85	3.55-04 / 11.74	— —	— —	— —
8	1.33-14 / 1.44	1.60-15 / 1.66	1.96-13 / 1.94	5.12-12 / 2.33	6.09-10 / 2.93	5.51-08 / 3.91	4.43-06 / 5.89	4.05-04 / 11.82	— —	— —
9	1.09-16 / 1.29	2.79-16 / 1.45	3.76-16 / 1.67	1.13-13 / 1.95	1.12-11 / 2.35	1.09-09 / 2.95	8.26-08 / 3.94	5.70-06 / 5.93	4.54-04 / 11.90	— —

* oscillator strength
** wavelength, microns

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Table 7-2. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO^+(A^4I-A^4I)$.

$v'\backslash v''$	0	1	2	3	4	5	6	7	8	9
*										
**										
10	5.76-15 / 1.16	6.08-16 / 1.30	2.52-14 / 1.46	6.99-16 / 1.68	1.71-13 / 1.96	2.23-11 / 2.36	1.83-09 / 2.96	1.18-07 / 3.97	7.11-06 / 5.97	5.03-04 / 11.98
11	3.15-15 / 1.06	4.22-15 / 1.17	6.91-15 / 1.30	1.51-14 / 1.47	6.23-16 / 1.69	4.62-13 / 1.98	4.11-11 / 2.38	2.89-09 / 2.98	1.62-07 / 3.99	8.68-06 / 6.01
12	6.74-17 / 0.98	3.02-15 / 1.07	2.45-17 / 1.18	9.66-15 / 1.31	2.43-15 / 1.48	4.03-15 / 1.70	8.43-13 / 1.99	7.03-11 / 2.40	4.31-09 / 3.00	2.16-07 / 4.02
13	1.38-15 / 0.90	3.28-16 / 0.98	1.10-16 / 1.07	4.87-16 / 1.19	3.77-15 / 1.32	2.85-15 / 1.49	6.66-15 / 1.71	1.22-12 / 2.00	1.14-10 / 2.41	6.21-09 / 3.02
14	5.03-16 / 0.84	4.00-15 / 0.91	2.00-16 / 0.99	4.01-15 / 1.08	1.53-17 / 1.19	3.91-15 / 1.33	1.12-14 / 1.50	3.42-15 / 1.72	2.11-12 / 2.02	1.76-10 / 2.43
15	3.18-18 / 0.79	1.31-15 / 0.85	1.59-15 / 0.92	5.18-16 / 0.99	2.21-15 / 1.09	1.28-15 / 1.20	1.11-14 / 1.34	1.02-14 / 1.51	2.01-15 / 1.74	3.59-12 / 2.03
16	1.72-16 / 0.74	2.18-16 / 0.79	1.10-15 / 0.85	8.78-18 / 0.92	6.02-16 / 1.00	6.48-17 / 1.10	1.23-15 / 1.21	1.44-14 / 1.35	1.17-14 / 1.52	5.07-15 / 1.75
17	1.27-16 / 0.70	1.15-15 / 0.75	1.86-16 / 0.80	1.03-18 / 0.86	3.90-16 / 0.93	7.85-16 / 1.01	1.57-16 / 1.10	2.39-15 / 1.22	1.24-14 / 1.36	1.80-14 / 1.53
18	1.39-17 / 0.66	3.63-16 / 0.70	2.07-15 / 0.75	6.70-17 / 0.80	4.14-16 / 0.86	2.90-17 / 0.93	6.65-16 / 1.01	4.58-16 / 1.11	3.79-15 / 1.23	1.50-14 / 1.37
19	1.19-17 / 0.63	3.26-18 / 0.67	9.08-16 / 0.71	7.91-16 / 0.76	1.80-18 / 0.81	3.01-16 / 0.87	2.51-16 / 0.94	1.13-15 / 1.02	8.19-17 / 1.12	3.05-15 / 1.23

* oscillator strength
** wavelength, microns

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Table 7-3. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of UO⁺(A⁴I-A⁴I).

v'\v''	0	1	2	3	4	5	6	7	8	9
20 * **	4.14-17 0.60	1.27-16 0.63	5.05-17 0.67	5.20-16 0.71	5.17-19 0.76	7.23-17 0.81	2.76-17 0.88	1.86-16 0.95	1.93-15 1.03	8.88-17 1.13
21	1.85-17 0.57	1.13-16 0.60	7.65-16 0.64	7.08-17 0.68	1.39-16 0.72	4.37-17 0.77	1.96-16 0.82	4.75-18 0.88	7.61-16 0.95	1.89-16 1.04
22	7.42-20 0.55	3.74-17 0.58	4.61-16 0.61	9.06-16 0.64	1.89-17 0.68	2.92-18 0.72	7.24-18 0.77	5.10-17 0.83	1.85-16 0.89	5.80-18 0.96
23	1.01-17 0.53	2.37-19 0.55	1.22-17 0.58	4.81-16 0.61	2.89-16 0.65	4.74-17 0.69	5.66-17 0.73	8.96-17 0.78	1.04-15 0.83	7.82-18 0.89
24	6.78-18 0.51	2.24-17 0.53	1.00-16 0.56	2.09-18 0.59	4.91-16 0.62	5.06-18 0.65	1.22-18 0.69	9.93-17 0.73	2.28-16 0.78	5.55-16 0.84
25	4.22-20 0.49	5.01-17 0.51	1.76-16 0.53	2.69-16 0.56	1.71-17 0.59	2.51-16 0.62	6.81-17 0.66	2.21-17 0.70	2.97-18 0.74	8.47-16 0.79
26	1.56-18 0.47	2.46-17 0.49	7.40-17 0.51	2.39-16 0.54	2.42-16 0.56	9.28-17 0.59	8.19-18 0.63	3.56-18 0.66	6.71-20 0.70	4.33-18 0.74
27	5.61-19 0.46	5.88-21 0.47	8.02-19 0.50	3.66-17 0.52	3.56-16 0.54	1.33-16 0.57	8.10-17 0.60	1.68-17 0.63	9.68-22 0.67	5.00-16 0.70
28	2.26-19 0.44	1.88-17 0.46	2.85-17 0.48	7.40-18 0.50	7.21-17 0.52	4.61-16 0.55	5.06-17 0.57	2.77-17 0.60	1.08-16 0.63	5.30-17 0.67
29	5.44-19 0.43	2.56-17 0.44	5.39-17 0.46	4.93-17 0.48	1.17-17 0.50	8.97-17 0.52	5.53-17 0.55	5.27-17 0.58	1.70-16 0.61	1.81-17 0.64

* oscillator strength
** wavelength, microns

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Table 7-4. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO^+(A^4I - A^4I)$.

V'\V"	10	11	12	13	14	15	16	17	18	19
10	– / –	– / –	– / –	– / –	– / –	– / –	– / –	– / –	– / –	– / –
11	* 5.51-04 / ** 12.06	– / –	– / –	– / –	– / –	– / –	– / –	– / –	– / –	– / –
12	1.04-05 / 6.05	5.99-04 / 12.14	– / –	– / –	– / –	– / –	– / –	– / –	– / –	– / –
13	2.81-07 / 4.05	1.23-05 / 6.09	6.47-04 / 12.22	– / –	– / –	– / –	– / –	– / –	– / –	– / –
14	8.69-09 / 3.04	3.57-07 / 4.07	1.43-05 / 6.13	6.94-04 / 12.30	– / –	– / –	– / –	– / –	– / –	– / –
15	2.64-10 / 2.44	1.19-08 / 3.06	4.46-07 / 4.10	1.65-05 / 6.17	7.41-04 / 12.38	– / –	– / –	– / –	– / –	– / –
16	5.78-12 / 2.04	3.84-10 / 2.46	1.59-08 / 3.09	5.48-07 / 4.13	1.88-05 / 6.21	7.88-04 / 12.47	– / –	– / –	– / –	– / –
17	8.97-15 / 1.76	9.50-12 / 2.06	5.42-10 / 2.48	2.07-08 / 3.11	6.66-07 / 4.16	2.13-05 / 6.26	8.34-04 / 12.55	– / –	– / –	– / –
18	1.70-14 / 1.54	1.66-14 / 1.77	1.30-11 / 2.08	7.62-10 / 2.49	2.64-08 / 3.13	7.99-07 / 4.18	2.39-05 / 6.30	8.80-04 / 12.64	– / –	– / –
19	1.62-14 / 1.38	7.44-14 / 1.55	5.91-14 / 1.78	1.80-11 / 2.09	1.03-09 / 2.51	3.36-08 / 3.15	9.47-07 / 4.21	2.67-05 / 6.34	9.26-04 / 12.73	– / –

* oscillator strength
** wavelength, microns

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Table 7-5. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO^+(A^4I-A^4I)$.

v'\v''	10	11	12	13	14	15	16	17	18	19
20 * **	1.54-14 1.24	2.21-14 1.39	1.21-13 1.56	3.58-14 1.79	2.84-11 2.10	1.35-09 2.53	4.21-08 3.17	1.11-06 4.24	2.96-05 6.39	9.71-04 12.82
21	7.81-16 1.13	1.35-14 1.25	8.43-14 1.39	7.21-14 1.57	9.87-15 1.81	4.16-11 2.11	1.78-09 2.55	5.19-08 3.19	1.30-06 4.27	3.26-05 6.43
22	9.99-16 1.04	1.02-14 1.14	6.14-15 1.26	1.36-13 1.40	1.22-13 1.59	7.68-14 1.82	5.49-11 2.13	2.33-09 2.56	6.34-08 3.22	1.50-06 4.31
23	6.46-17 0.97	3.81-16 1.05	4.78-15 1.15	3.25-14 1.27	9.08-14 1.41	3.16-13 1.60	2.20-13 1.83	7.35-11 2.14	2.96-09 2.58	7.67-08 3.24
24	4.76-16 0.90	2.40-15 0.97	2.58-15 1.06	2.59-17 1.16	7.63-14 1.28	1.19-13 1.42	4.44-13 1.61	2.14-13 1.84	9.85-11 2.16	3.73-09 2.60
25	8.70-18 0.84	6.09-16 0.91	2.86-15 0.98	1.43-15 1.06	5.53-15 1.17	7.10-14 1.29	2.89-13 1.43	5.93-13 1.62	2.75-13 1.86	1.25-10 2.17
26	4.05-17 0.79	7.28-16 0.85	1.28-15 0.91	3.78-16 0.99	1.75-16 1.07	3.41-14 1.18	9.93-14 1.30	4.53-13 1.44	1.04-12 1.63	3.75-13 1.87
27	2.90-16 0.75	2.64-16 0.80	2.12-15 0.85	2.16-15 0.92	1.75-15 0.99	1.32-15 1.08	4.49-14 1.18	2.10-13 1.31	7.13-13 1.46	1.29-12 1.64
28	1.27-16 0.71	1.19-17 0.75	6.88-16 0.80	2.25-17 0.86	5.04-16 0.93	1.21-16 1.00	1.42-14 1.09	8.02-14 1.19	2.63-13 1.31	1.21-12 1.47
29	7.18-16 0.67	2.83-16 0.71	4.25-16 0.76	4.27-15 0.81	1.54-16 0.87	2.63-15 0.93	2.31-15 1.01	1.68-14 1.10	1.36-13 1.20	4.11-13 1.32

* oscillator strength
** wavelength, microns

Table 7-6. Calculated oscillator strengths ($f_{v'v''}$) for the vibrational-rotational transition of $UO^+(A^4I-A^4I)$.

v'\v"		20	21	22	23	24	25	26	27	28	29
20	*	—	—	—	—	—	—	—	—	—	—
	**	—	—	—	—	—	—	—	—	—	—
21	*	1.02-03	—	—	—	—	—	—	—	—	—
	**	12.91	—	—	—	—	—	—	—	—	—
22	*	3.59-05	1.06-03	—	—	—	—	—	—	—	—
	**	6.48	13.00	—	—	—	—	—	—	—	—
23	*	1.73-06	3.92-05	1.11-03	—	—	—	—	—	—	—
	**	4.33	6.52	13.10	—	—	—	—	—	—	—
24	*	9.18-08	1.97-06	4.27-05	1.15-03	—	—	—	—	—	—
	**	3.26	4.37	6.57	13.19	—	—	—	—	—	—
25	*	4.67-09	1.09-07	2.24-06	4.63-05	1.19-03	—	—	—	—	—
	**	2.62	3.29	4.40	6.62	13.29	—	—	—	—	—
26	*	1.64-10	5.74-09	1.29-07	2.53-06	5.01-05	1.24-03	—	—	—	—
	**	2.19	2.64	3.31	4.43	6.67	13.39	—	—	—	—
27	*	3.00-13	2.16-10	7.02-09	1.52-07	2.85-06	5.41-05	1.28-03	—	—	—
	**	1.88	2.21	2.66	3.33	4.46	6.72	13.49	—	—	—
28	*	1.64-12	4.35-13	2.74-10	8.55-09	1.77-07	3.19-06	5.81-05	1.32-03	—	—
	**	1.66	1.90	2.22	2.68	3.36	4.50	6.77	13.59	—	—
29	*	1.52-12	2.46-12	7.39-13	3.48-10	1.04-08	2.05-07	3.56-06	6.23-05	1.36-03	—
	**	1.48	1.67	1.91	2.24	2.70	3.38	4.53	6.82	13.69	—

  * oscillator strength
  ** wavelength, microns

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Table 8. Total integrated absorption coefficients for UO^+ ground state.

$$\text{Absorption Coefficient, } cm^{-2} atm^{-1}$$

Temperature, °K (Wavelength, μ)	Fundamental (11.30)	First Overtone (5.67)	Second Overtone (3.79)	Third Overtone (2.85)	Total
100.	1230.827	3.810	.023	.000	1234.660
273.15	1230.764	3.882	.024	.000	1234.670
300.	1230.729	3.921	.024	.000	1234.674
500.	1230.215	4.458	.974	.000	1235.647
1000.	1227.852	6.782	.061	.001	1234.696
1500.	1224.990	9.549	.117	.002	1234.658
2000.	1221.961	12.462	.197	.004	1234.624
2500.	1218.825	15.449	.302	.008	1234.584
3000.	1215.540	18.485	.433	.013	1234.471
4000.	1208.159	24.668	.777	.032	1233.636
5000.	1199.135	30.928	1.229	.063	1231.355

REFERENCES

1. Harang, O., "AlO Resonant Spectrum for Upper Atmosphere Temperature Determination," AFCRL-66-314, Environmental Research Paper, No. 192, 1966.

2. Churchill, D. R. and R. E. Meyerott, "Spectral Absorption in Heated Air," Journal of Quantitative Spectroscopy and Radiative Transfer, 5, p. 69, 1965.

3. The Airglow and the Aurorae, edited by E. B. Armstrong and A. Dalgarno. Pergamon Press, New York, 1955.

4. Armstrong, B. H., R. R. Johnston and P. S. Kelly,"The Atomic Line Contribution to the Radiation Absorption Coefficient of Air," Journal of Quantitative Spectroscopy and Radiative Transfer, 5, p. 55, 1965.

5. Johnston, R. R., B. H. Armstrong and O. R. Platas, "The Photoionization Contribution to the Radiation Absorption Coefficient of Air," Journal of Quantitative Spectroscopy and Radiative Transfer, 5, p. 49, 1965.

6. Michels, H. H. and F. E. Harris, "Valence Configuration Interaction Calculations for Atomic Scattering," International Journal of Quantum Chemistry, IIS, p. 21, 1968.

7. Harris, F. E. and H. H. Michels, "Open-Shell Valence Configuration - Interaction Studies of Diatomic and Polyatomic Molecules," International Journal of Quantum Chemistry, IS, p. 329, 1967.

8. Michels, H. H., "Molecular Orbital Studies of the Ground and Low-Lying Excited States of the HeH$^+$ Molecular Ion," Journal of Chemical Physics, 44, p. 3834, 1966.

9. Michels, H. H., "Ab Initio Calculation of the $B^2\Sigma^+ - X^{2+}\Sigma$ Oscillator Strengths in AlO," Journal of Chemical Physics, 56, p. 665, 1971.

10. Michels, H. H., "Calculation of Electronic Wavefunctions," Final Report for AFOSR Contract F44620-74-C-0083, August 1975.

11. Michels, H. H., "Calculation of Potential Energy Curves for Metal Oxides and Halides," Final Report for AFOSR, Contract F44620-73-C-0077, May 1977.

12. Michels, H. H., "Theoretical Determination of Metal Oxide f-Numbers," Final Report for AFWL, Contract F29601-71-C-0119, Report AFWL-TR-74-239, May 1975.

REFERENCES (Cont'd)

13. Schaefer, F. E. and F. E. Harris, "Ab Initio Calculations of 62 Low-Lying States of the O_2 Molecule," Journal of Chemical Physics, 48, p. 4946, 1968.

14. Michels, H. H. and F. E. Harris, "Predissociation Effects in the $A^2\Sigma^+$ State of the OH Radical," Chemical Physics Letters, 3, p. 441, 1969.

15. Harris, F. E., "Open-Shell Orthogonal Molecular Orbital Theory," Journal of Chemical Physics, 46, p. 2769, 1967.

16. Roothan, C. C. J. and P. S. Bagus, "Atomic Self-Consistent Field Calculations by the Expansion Method," Methods in Computational Physics. Edited by B. Alder, 2, p. 47, 1963.

17. Givens, W., "Eigenvalue-Eigenvector Techniques," Oak Ridge Report Number ORNL 1574 (Physics).

18. Shavitt, I., C. F. Bender, A. Pipano, and R. P. Hosteny, "The Iterative Calculation of Several of the Lowest or Highest Eigenvalues and Corresponding Eigenvectors of Very Large Symmetry Matrices," Journal of Computational Physics, 11, p. 90, 1973.

19. Harris, F. E. and H. H. Michels, "The Evaluation of Molecular Integrals for Slater-Type Orbitals," 13, p. 205, 1967.

20. Davidson, E. R., "Natural Expansion of Exact Wavefunctions, III. The Helium Atom Ground State," Journal of Chemical Physics, 39, p. 875, 1963.

21. Wahl, A. C., P. J. Bertoncini, G. Das and T. L. Gilbert, "Recent Progress Beyond the Hartree-Fock Method for Diatomic Molecules, The Method of Optimized Valence Configurations," International Journal of Quantum Chemistry, IS, p. 123, 1967.

22. Slater, J. C., Advances in Quantum Chemistry, 6, p. 1, 1972.

23. Löwdin, P. O., "Quantum Theory of Many-Particle Systems. I. Physical Intepretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction," Physical Review, 97, p. 1474, 1955.

REFERENCES (Cont'd)

24. Kohn, W. and L. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects," Physical Review, 140A, p. 1133, 1965.

25. Slater, J. C., "A Simplification of the Hartree-Fock Method," Physical Review, 81, p. 385, 1951.

26. Schwarz, K.: "Optimization of the Statistical Exchange Parameters α for the Free Atoms H Through Nb," Physical Review, B5, p. 2466, 1972.

27. Beebe, N. H. F., "On the Transition State in the X_α Method," Chemical Physics Letters, 19, p. 290, 1973.

28. Schwarz, K. and J. W. D. Connolly, "Approximate Numerical Hartree-Fock Method for Molecular Calculations," Journal of Chemical Physics, 55, p. 4710, 1971.

29. Connolly, J. W. D: unpublished results.

30. Slater, J. C., "Hellmann-Feynman and Virial Theorems in the X_α Method," Journal of Chemical Physics, 57, p. 2389, 1972.

31. Michels, H. H., R. H. Hobbs and J. C. Connolly, "Optimized SCF-X_α Procedures for Heterpolar Molecules," Journal of Chemical Physics (to be published).

32. Rosch, Notker and Keith H. Johnson, "On the Use of Overlapping Spheres in the SCF-X_α Scattered-Wave Method," Chemical Physics Letters, 23, p. 149, 1973.

33. Heitler, W., The Quantum Theory of Radiation. 3rd Edition, Oxford University Press, 1953.

34. Nicholls, R. W. and A. L. Stewart, Allowed Transitions. Atomic and Molecular Processes, D. R. Bates, Editor. Academic Press, 1962.

35. Penner, S. S., Quantitative Molecular Spectroscopy and Gas Emissivities, Addison-Wesley Publishing Company, Inc., 1959.

36. Dennison, D. M., "The Rotation of Molecules," Physical Review, 28, p. 318, 1926.

37. Kronig, R. and I. Rabi, "The Symmetrical Top in the Undulatory Mechanics," Physical Review, 29, p. 262, 1927.

REFERENCES (Cont'd)

38. Rademacher, H. and F. Reiche, "Die Quantelung des symmetrischen Kreisels nach Schrodingers Undulationsmechanik," Zeitschrift fur Physik, 41, p. 453, 1927.

39. Hönl, H. and F. London, "Intensities of Band Spectrum Lines," Zeitschrift fur Physik, 33, p. 803, 1925.

40. Herzberg, G., Spectra of Diatomic Molecules. 2nd Edition, Van Nostrand, 1950.

41. Fraser, P. A., "A Method of Determining the Electronic Transition Moment for Diatomic Molecules," Canadian Journal of Physics, 32, p. 515, 1954.

42. Breit, G., "The Effect of Retardation on the Interaction of Two Electrons." Physical Review, 34, p. 553, 1929; "The Fine Structure of He as a Test of the Spin Interactions of Two Electrons," 36, p. 383, 1930; "Dirac's Equation and the Spin-Spin Interactions of Two Electrons," 39, p. 616, 1932.

43. Bethe, H. A. and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms. Academic Press, N. Y., 1957.

44. Hirschfelder, J. O., C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids. John Wiley, N. Y., 1964.

45. Itoh, T., "Derivation of Nonrelativistic Hamiltonian for Electrons from Quantum Electrodynamics," Reviews of Modern Physics, 37, p. 159, 1965.

46. Kolos, W. and L. Wolniewicz, "Accurate Adiabatic Treatment of the Ground State of the Hydrogen Molecule," Journal of Chemical Physics, 41, p. 3663, 1964; "Accurate Computation of Vibronic Energies and Some Expectation Values for H_2, D_2, and T_2," 41, p. 3674, 1964; "Potential-Energy Curve for the $B^1\Sigma u^+$ State of the Hydrogen Molecule," 45, p. 509, 1966.

47. Liberman, D., J. T. Waber, D. T. Cromer, "Self-Consistent Field Dirac-Slater Wave Functions for Atoms and Ions. I. Comparison with Previous Calculations," Physical Review, A137, p. 27, 1965.

48. Mann, J. B. and J. T. Waber, "SCF Relativistic Hartree-Fock Calculations on the Superheavy Elements 118-131," Journal of Chemical Physics, 53, p. 2397, 1970.

REFERENCES (Cont'd)

49. Grant, I. P.: "Relativistic Calculation of Atomic Structures," Advances in Physics, 19, p. 747, 1970.

50. Cowan, R. D.: "Atomic Self-Consistent-Field Calculations Using Statistical Approximations for Exchange and Correlation," Physical Review, 163, p. 54, 1967.

51. Desclaux, J. P., D. F. Mayers, and F. O'Brien, " Relativistic Atomic Wave Functions," Journal of Physics B, 4, p. 631, 1971.

52. Cowan, R. D. and D. C. Griffin, "Approximate Relativistic Corrections to Atomic Radial Wave Functions," Journal of the Optical Society of America, 66. p. 1010, 1976.

53. Wood, J. H. and A. M. Boring: "Improved Pauli Hamiltonian for Local-Potential Problems," Physical Review B, 18, p. 2701, 1978.

54. Boring, A. M. and J. H. Wood, "Relativistic Calculations of the Electronic Structure of UF_6," Journal of Chemical Physics, 71, p. 32, 1979.

55. Wood, J. H., A. M. Boring and S. B. Woodruff, "Relativistic Electronic Structure of UO_2^{++}, UO_2^{+} and UO_2," Journal of Chemical Physics, 74, p. 5225, 1981.

56. Michels, H. H., R. H. Hobbs and J. W. D. Connolly, "Electronic Structure and Photoabsorption of the Hg_2^{+} Dimer Ion," Chemical Physics Letters, 68, p. 549, 1979.

57. Weeks, J. D., A. Hazi and S. A. Rice: Advances in Chemical Physics, 16, p. 283, 1969.

58. Bardsley, J. N.: Case Studies in Atomic Physics. 4 p. 299, 1974.

59. Phillips, J. C. and L. Kleinman, "New Method for Calculating Wave Functions in Crystals and Molecules," Physical Review, 116, p. 287, 1959.

60. Hazi, A. U. and S. A. Rice, "Pseudopotential Theory of Atomic and Molecular Rydberg States," Journal of Chemical Physics, 45, p. 3004, 1966.

REFERENCES (Cont'd)

61. Tully, J. C., "Many-Electron Pseudopotential Formalism for Atomic and Molecular Excited-State Calculations," Physical Review, 181, p. 7, 1969.

62. Melius, C. F., B. D. Olafson and W. A. Goddard III, "Fe and Ni Ab Initio Effective Potentials for Use in Molecular Calculations," Chemical Physics Letters, 28, p. 457, 1974.

63. Szasz, L. and G. McGinn, "Atomic and Molecular Calculations With The Pseudopotential Method. II. Exact Pseudopotentials for Li, Na, K, Rb, Be^+, Mg^+, Ca^+, Al^{++}, Cu and Zn^+," Journal of Chemical Physics, 47, p. 3495, 1967; "Atomic and Molecular Calculations with the Pseudopotential Method III: The Theory of Li_2, Na_2, K_2, LiH, NaH and KH; Pseudopotential Theory of Atoms and Molecules. II. Hylleraas-Type Correlated Pair Functions for Atoms With Two Valence Electrons," 56, p. 1019, 1972.

64. Kahn, L. R., P. Baybutt and D.G. Truhlar, "Ab Initio Effective Core Potentials: Reduction of All-Electron Molecular Structure Calculations to Calculations involving Only Valence Electrons," Journal of Chemical Physics, 65, p. 3826, 1976.

65. Lee, Y. S., W. C. Ermler and K. S. Pitzer, "Ab Initio Effective Core Potentials Including Relativistic Effects. I. Formalism and Applications to the Xe and Au Atoms," Journal of Chemical Physics, 67, p. 5861, 1977.

66. Cowiant, R. and D. Hilbert, Methods of Mathematical Physics, Interscience, N. Y., 1961.

67. Froese-Fischer, C., Comp. Phys. Comm. 1, p. 151, 1969.

68. Kahn, L. R., P. J. Hay and R. D. Cowan, "Relativistic Effects in Ab Initio Effective Core Potentials for Molecular Calculations. Applications to the Uranium Atom," Journal of Chemical Physics, 68, p. 2386, 1978.

69. Desclaux, J. P.: Atomic Data and Nuclear Tables, 12, p. 311, 1973.

70. Krauss, M. O.: private communication.

71. Herman, F. and S. Skillman, Atomic Structure Calculations. Prentice-Hall, New Jersey, 1963.

REFERENCES (Cont'd)

72. Layzer, D., "On A Screening Theory of Atomic Spectra," _Annals of Physics_, 8, p. 271, 1959.

73. Kiess, C. C., C. J. Humphreys and D. D. Laung, _J. Res. National Bureau of Standards_, 37, p. 57, 1946.

74. Elliott, J. P., B. R. Judd and W. A. Runciman, "Energy Levels in Rare-Earth Ions," _Proceeding of the Royal Society_, A240, p. 509, 1957.

75. Judd, B. R., "Low-Lying Levels in Certain Actinide Atoms," _Physical Review_, 125, p. 613, 1962.

76. Hulburt, H. M. and J. O Hirschfelder, "Potential Energy Functions for Diatomic Molecules," _Journal of Chemical Physics_, 9, p. 61, 1941.

77. Krauss, M. O. and W. S. Stevens, "The Electronic Structure and Spectra of UO^+," _Chemical Physics Letters_, to be published 1983.

78. McGlynn, S. P. and J. K. Smith, "Electronic Structure, Spectra, and Magnetic Properties of Actinyl Ions. II. Neptunyl and the Ground States of Other Actinyls," _Journal of Molecular Spectroscopy_, 6, p.188, 1961.

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